ANALYTICAL AND CHEMOMETRIC APPLICATIONS IN THE STUDY OF AUTOMOTIVE AND RELATED LUBRICANT DEGRADATION

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BSc (Hons)

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DEDICATION

This work is dedicated to my wonderful parents, who have provided endless support and encouragement. To my late Father who did not foresee the future, and enthusiastically looked forward to the completion of this work.

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I am indebted to my Fiancé, Dele for his inspiration, understanding and support throughout this work.

Abstract

Chemometric techniques have been utilised for the study of automotive lubricant oil degradation. The initial investigations were performed by analysis of data from top ring zone engine test datasets. Principal component analysis (PCA) was used to explore the ring zone data. The difference in the performance of various lubricant formulations sampled from the ring zone region of operating Petter AA-1 diesel and Petter W-1 petrol engines was established by the partial least squares discriminant model (PLS-DA). The results from the study of the test engine data provided optimised insight into the break down of the chemical/physical parameters of the lubricants during operative conditions.

This work proceeded onto condition monitoring techniques. Over a hundred used oil samples were obtained from the sump of various petrol and diesel engine vehicles, in addition fresh oil samples were also collected. Series sets of used oil samples were acquired by periodic sampling from a Honda 1.8 L petrol engine, a Peugeot 1.9 L diesel engine and a diesel engine sump test. Following sample acquisition, each oil sample was analysed using FTIR/ATR and conductimetric titrations were performed. These analytical equipments are used to monitor and assess the extent of degradation.

A novel model was developed to enhance the IP 400 conductimetric titration method of measuring base number of new and used lubricants. This nonlinear least-squares model was integrated into the titration programme along with two linear least-squares curve fitting methods. The models were effectively used to estimate the titration endpoint which was subsequently used in base number calculation. The results demonstrated the robustness of the three endpoint estimation methods and indicate reliability of the titration equipment and programme.

PCA was used to analyse the FTIR spectra data of the oil samples. PCA performed on different sets of pre-processed data uncovered objective information on the condition of the lubricants. PCA models of the series set oil samples highlighted difference between samples as a result of progressive degradation. The effect of adding fresh oil (top-up) to the engine was apparent.

This work has demonstrated the importance and efficiency of mathematical/statistical models in lubricant oil engine testing and condition monitoring.

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Rationale

Lubricants are used to prevent or delay the onset of wear due to friction between surfaces; whlist acting as a coolant by heat elimination. The performance requirements of lubricant systems are complex and their formulations have many components which are incorporated to perform these varied functions. The lubricant system becomes even more complex when in service, due to continuous changes in its chemical and physical properties. To improve on the partial understanding of how lubricants degrade in service, numeric analytical techniques such as chemometrics are employed.

Chemometrics are mathematical/statistical procedures utilized for analysis of chemical data. The aim is to provide optimal insight into a chemical system. These techniques are effective for multivariate data, where multiple parameters measured on multiple samples at numerous time points can be simultaneously analysed. Furthermore multi-variation is a characteristic procedure in engine lubrication assessment.

For this reason the application of mathematical analytical solutions are essential and valuable in the studies of lubricant degradation and fluid behaviour.

This is the rationale for this research work.

Chapter 1

Automotive Engines and Lubrication

1.1 Introduction to the Internal Combustion Engine

Before the invention of wheeled vehicles, animals were tamed and trained to carry heavy loads and travel distances at speed greater than man can, while heavier loads were dragged upon sledges until the invent of wheels and rails. As manufacturing technology advanced wheeled vehicles where continuously improved. The development of steam engines led to its application to vehicles in the eighteenth century; however, it proved more suitable to railway vehicles (locomotives) than for road vehicles.

A **steam engine** converts the heat energy of pressurised steam into mechanical work. The heat produced by an external combustion source is used to raise steam, which forces the piston to move in and out of its stroke in the cylinder.

Towards the end of the nineteenth century, the successful development of the internal combustion engine[1] led to power driven vehicles such as motor cars, buses and trucks which have become an integral part of the modern society.

The **internal combustion engine (ICE)** is a heat engine which depends on the exothermic chemical process of combustion (reaction of fuel with air) which occurs inside the cylinder of the engine. The most common fuels are made of hydrocarbons such as diesel and petrol. The expansion of the hot gas produced directly provides mechanical power that forces the piston to move up and down (reciprocating) or generate a rotary movement (rotary engines, turbines,). Internal combustion engines are used for almost all passenger cars, motorbikes, and many air and sea transportation devices due to its performance, versatility and reliability.

The reciprocating internal combustion engine as shown in Figure 1 is the most important component in a motor vehicle[2].

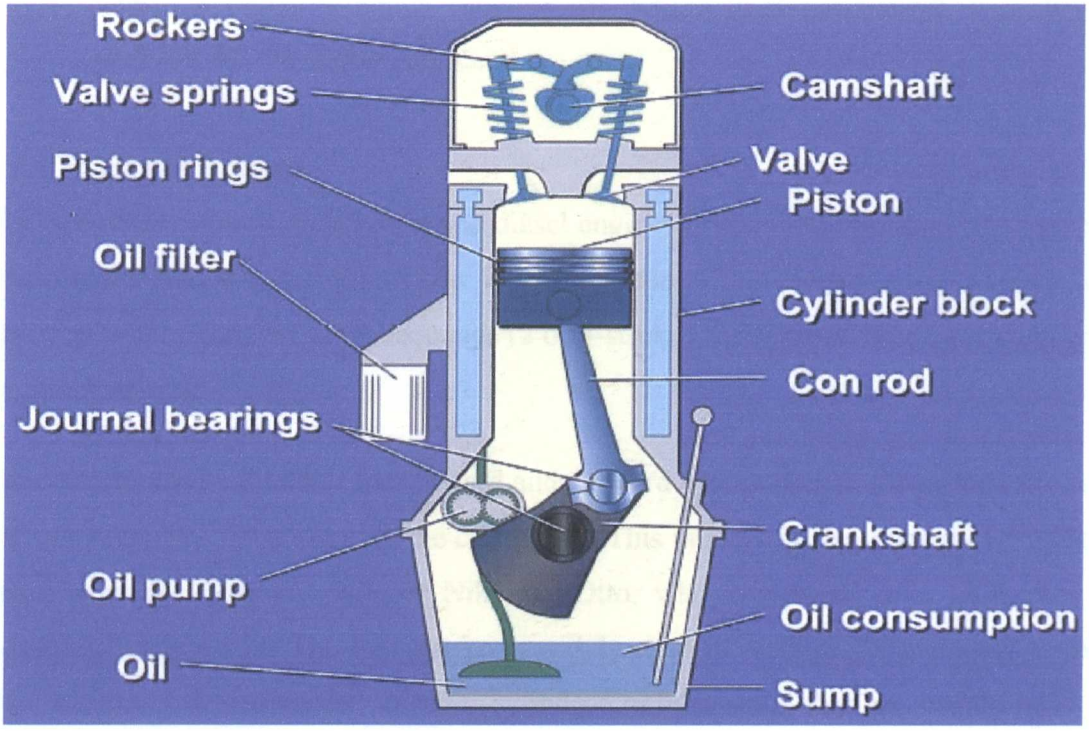


Figure 1: Components of an internal combustion engine

The main engine components and their names are described below.

- **Cylinder block**: a structure used to guide and support the piston. It also houses the liquid coolant.
- **Crankshaft**: consists of a circular sectioned shaft which is bent to form two perpendicular crank-arms and a big-end journal. The unbent part of the shaft provides the main journal and the crankshaft is indirectly linked by the connecting rod to the piston, which enables the linear motion of the piston to be transformed into rotary motion.
- **Connecting rod (Con rod)**: a link-rod that transmit the pressure impulses acting on the piston to the crankshaft big-end journal.
- **Piston**: pressure tight cylindrical plunger which converts the gas pressure from the combustion into a driving thrust along the connecting rod.
- **Piston ring**: circular rings that seal the gaps between the piston and the cylinder. They aim to prevent the gas escape and control the amount of lubricant which lubricates the top of the cylinder.

- **Sump**: a container which encloses the bottom of the crankcase. It is also a reservoir for the engine lubricant.

1.1.1 Engine Operation

The operating cycle of most petrol and diesel engines is based on "**strokes**"; an upward or downward motion of the piston in the cylinder. The reciprocating engines are characterised by their working sequence (2 or 4-stroke) and ignition type (spark ignition or compression).

Four-stroke cycle: involves four inward and outward movements of the piston (strokes) per two complete revolutions of the crankshaft. This process is also known as the **Otto cycle**, after the German engineer Nikolaus Otto, who introduced it in 1876 after a successful experiment. The four-stroke is widely used in most modern engines today; they are easily manufactured in multi-cylinder configurations that are mostly used in cars. The diagram given in Figure 2 below illustrates the mode of operation.

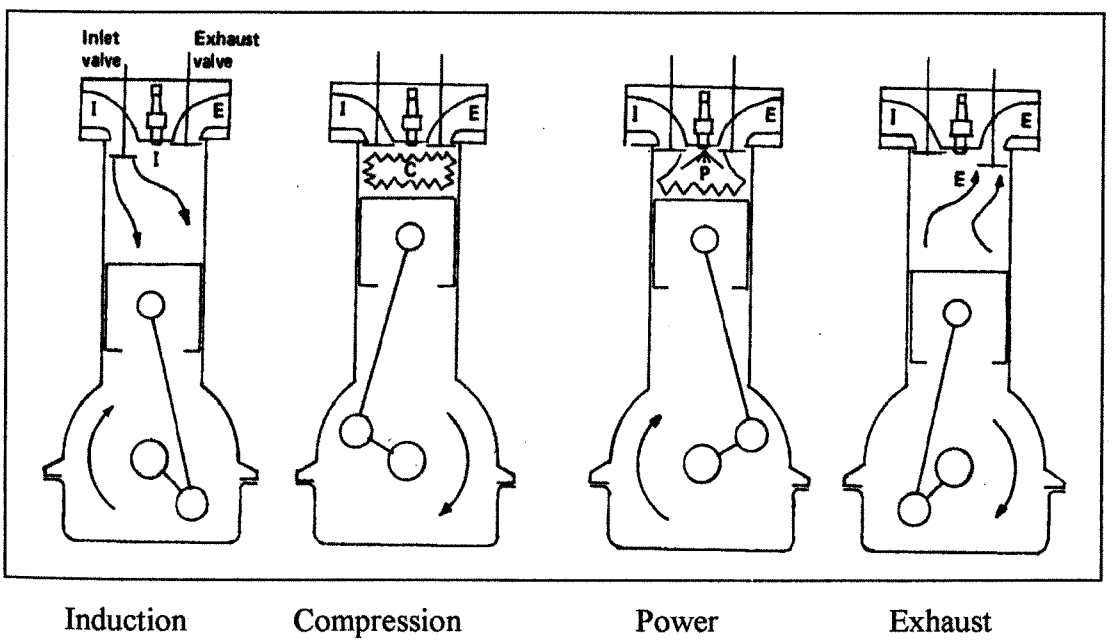


Figure 2: Diagram illustrates four-stroke cycle of a petrol engine[3]

1. First stroke (intake); is the induction stroke. The piston moves down with the inlet valve open, filling the cylinder with a mixture of fuel and air.
2. Second stroke; known as the compression stroke. The piston moves back up compressing the air/fuel mixture into the combustion chamber at the top end of the cylinder. Just before the end of the compression stroke, the spark plug screwed into the end of the cylinder emits an electrical spark which ignites the fuel vapour.
3. Third stoke; is the power stroke. The fuel burns rapidly heating the gas in cylinder to high temperatures and increasing pressure. The pressure forces the piston down the cylinder transmitting a turning effect to the crankshaft.
4. Fourth stroke; is the exhaust stroke. As the piston reaches the bottom of the stroke, the exhaust valve opens releasing the burnt fuel from the cylinder as the piston returns up the cylinder.

Although larger four stroke engines usually include more than one cylinder and various arrangements for the camshaft such as feature fuel injection, turbochargers, and multiple valves, the basic operation of the engine remains the same.

Two-stroke cycle: requires one inward and outward movement of the piston with one full revolution of the crankshaft. The operating procedure for this type of engine is summarised below.

In small two-strokes the crankcase as well as the cylinder is used to achieve the process of the cycle. As the piston begins to move upward, a fresh fuel/air mixture is drawn from the carburettor into the crankcase by the vacuum created during the upward stroke and at the same time compresses the fresh fuel mixture on top of the cylinder above the piston. The compressed mixture is ignited in the same way as in the four-stroke engine and the resulting high pressure of the hot gases drives the piston down on its second stroke. As the piston moves down, it compresses the fuel mixture in the crankcase and as it approaches the bottom of it's stroke it uncovers the exhaust port, allowing the burnt fuel to escape out of the cylinder. Shortly afterwards the transfer port opens to admit fresh fuel/air mixture into the cylinder from the crankcase. The momentum of the flywheel starts driving the piston upward on its next stroke and the cycle begins again. The cycle of operation is shown in Figure 3a.

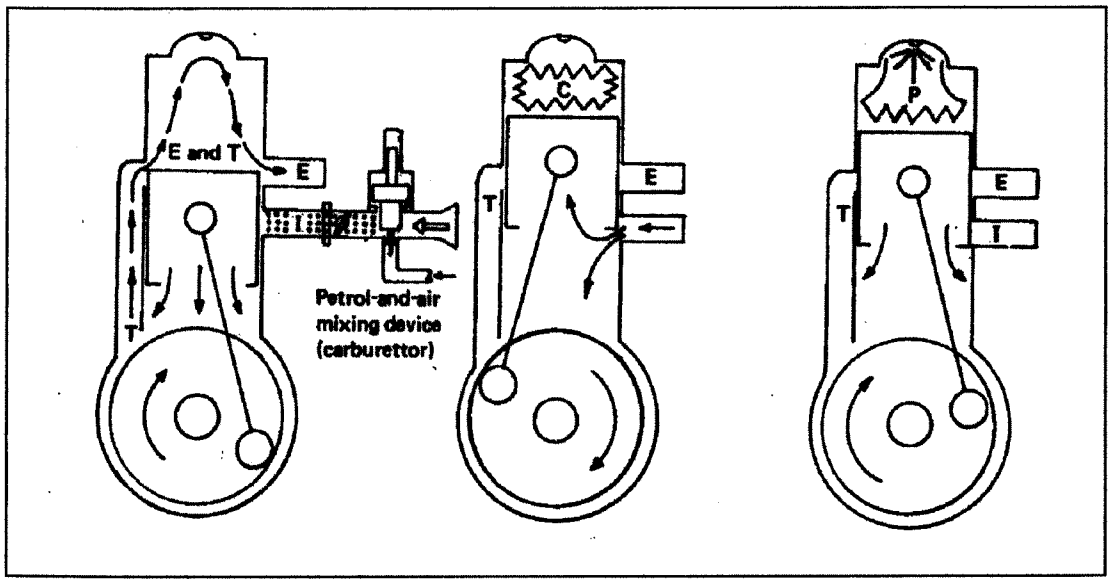


Figure 3a: Illustration of two-stroke cycle of a petrol engine[3]

The two-stroke engine is simpler mechanically and lighter in weight than the four-stroke engine. Since the two-stroke engine delivers one power stroke every two strokes, it develops more power than a four-stroke engine of the same size. For these reasons it is commonly used in lawn mowers, chain saws, jet-skies and motorcycles.

However some disadvantages restrict the use of two-stroke for petrol engine vehicles. Since there are twice as many power strokes during the operation the engine tends to heat up and therefore likely to have a shorter life. Also the two-stroke engine has a simple lubricating system in which oil is mixed with the fuel; this mixture lubricates the crankshaft, connecting rod and cylinder walls. Since the crankcase serves as pressurization chamber that forces air/fuel into the cylinder it is unable to hold thick oil. Due to the lack of a dedicated lubrication system the parts of a two-stroke engine wear much faster. In addition the two-stroke engine produces a lot of pollution due to very high level of hydrocarbons in its exhaust.

There are other types of two-stroke engines which are of industrial importance; these are used for large commercial engines such as marine engines, locomotives and industrial power plants.

In the two-stroke diesel a compressor is used to supply fresh scavenging air into the cylinder; in addition a turbo/supercharger is used to assist in the scavenging process and increase efficiency. Scavenging involves introducing fresh air into the cylinder and expelling burnt gases. The principle of operation is illustrated in Figure 3b below.

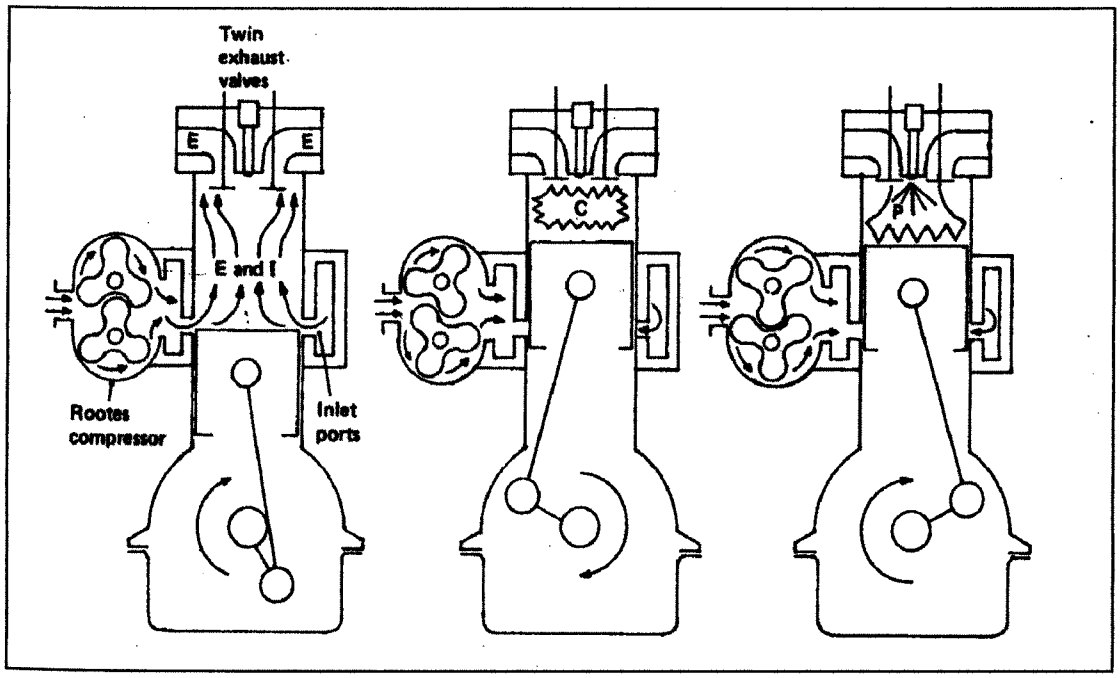


Figure 3b: Two-stroke cycle of a diesel engine[3]

This two-stroke diesel engine is twice as powerful and similarly efficient as a four-stroke equivalent engine. Since only air is expelled out of the exhaust valve and there is no mixing of lubricant with the fuel, pollution problems are not necessarily associated with this type of engine.

The various components of the engine, modes of operation and the numerous moving contacts in an engine, particularly as the piston moves through its strokes requires lubricating. Therefore, lubrication is essential and important for easy movements and protection of these parts against wear.

1.2 Introduction to Lubrication

The advent of lubricants is as old as mankind, an art that dates back to ancient times where the Egyptians used animal fats as greases and water as lubricants when moving large building blocks. The scientific focus on lubricants began in the 17th century with the development of axles and bearings. The development of automobiles and steam engines spurred development of modern lubricants consisting of base oils and chemical additives. However the detailed chemistry of lubricants was not fully understood, until recent advances in analytical instruments and techniques which offered unprecedented opportunities for analysing them. Subsequently large varieties of lubricants now exist; manufacturers are able to supply scores of different mineral oils, synthetic oils and polymers with specially developed additive packages. Hence one of the several available types of lubricants can now lubricate many machines satisfactorily.

Lubricants are very important industrial products and continue to develop at an ever-increasing rate as machinery and automotive technology progress. Consequently petroleum and automotive industries face growing government regulations on product efficiency, fuel economy, lower emissions and rapid technological changes required to improve performance[4-6].

Recognising the demands and constraints placed on today's lubricants, this thesis establishes the need for and demonstrates the application of analytical methods coupled with chemometric techniques for the study of chemical degradation of lubricants in service. This combination offers a novel approach to condition monitoring and analysis of the consequential data obtained from several oil testing procedures.

1.2.1 Requirements of a Lubricant

The category of lubricant required is defined by its applications. Lubricants can be solids, liquids or grease; however they must all be able to flow easily and perform vital functions. Lubrication of an engine is a complex process; motor oil must perform many functions under severe service conditions, such as these basic functions:

- provide a barrier between moving parts to reduce friction and wear;
- endure extreme conditions and resist build up of sludge and varnish;
- stay as a fluid in cold weather and remain thick enough to work in hot weather;

- provide a protective coating on all parts against rust and corrosion;
- act as a coolant which disperses heat arising from the combustion process and friction;
- neutralise acids that can build up and destroy polished metal surfaces;
- absorb and suspend dirt and carbon particles.

The kinds of lubricant, which are of interest in this study, are the lubricating oils for automotive engines, particularly diesel and petrol engines. The requirements for these lubricants are habitually driven by government legislation, specification standards and manufacturer requirements.

1.2.2 Defining Lubricant Performance

New legislation and technology designs instigate the production of the new lubricants. However before the formulation process, an assessment of what is required and what must be avoided is first established. The vehicle manufacturer or a generic classification system developed by groups of vehicle manufacturers in co-operation with the lubricant industries often present these requests as "**performance requirements**". The most widely used systems are:

- ACEA (Association des Constructeur Europeén d'Automobile) system from Europe;
- International Lubricant Standardization and Approval Committee (ILSAC);
- API (American Petroleum Institute) system from North America;
- JASO (Japan Automobile Standards Organisation) system from Japan;
- IP (Institute of Petroleum) system from UK.

The API originated in the 1930s and it is the traditionally known system. It is the sole definition of oil quality specified by the North American vehicle manufacturers and is often used to define acceptable quality throughout the rest of the world. The API system is based on three organisations working co-operatively. They are the SAE (Society of Automotive Engineers) who represent the vehicle manufacturers, the API

(American Petroleum Institute) who represent the oil industry and the ASTM (American Society for Testing Materials) who represent the scientific community.

The system operates as follows; when SAE demonstrates the need for a new lubricant, this prompts the ASTM to develop a test that simulates the problem. Once the developed test demonstrates significance, proves repeatable and reproducible then SAE establishes pass/fail criteria for accepting the performance. The API subsequently establish a new performance level which the lubricant companies develop lubricants to meet, and finally the vehicle manufacturers can specify the use of this lubricant quality for vehicle maintenance.

There are also other lubricant approval systems such as the US Military (MIL-L46152 and 2104), NATO, European and other countries requirements. Customers who are not satisfied with the API or ACEA certification system and wish to be assured by other independent bodies sometimes require these specifications.

SAE Oil Classification

When the SAE took the task of setting the standards for engine oil, they decided to compare and define lubricating oils by viscosity. Habitually viscosity and viscosity index are vital for selecting engines oils. To establish a simpler means for identification of lubricant they developed SAE J300[8] classification that specifies:

- viscosity at low temperatures, defines the W (winter) grades e.g. SAE 5W;
- and viscosity at high temperatures (100°C) defines the main grades (i.e. non-W) e.g. SAE 20.

The earliest engine oils were the non-W single grades; but as requirements for lubricants to perform better under miscellaneous conditions evolved, multigrade oils emerged. Oils that meet the W or non-W grade are called '**Single grades**', e.g. SAE 30 or SAE 10W while those that meet the requirements of both are called '**Multigrades**' e.g. SAE 5W-30. The main difference between them is that the multigrades exhibit greater viscosity stability over a wide range of temperatures than the single grade oils.

Since the advent of multigrade oils, the average engine oil demand for a vehicle has been reduced from 21.6 kg in 1972 to 13.3 kg in 1982, and currently to about 7.8 kg per year for personal cars[7].

API Service Classification

The viscosity of the lubricant alone is not enough to provide a guide to the likely behaviour of oil in an engine. Furthermore specific characteristics of an oil can change considerably with the inclusion of additives. In 1952, the API launched the service classifications system which, grades oils according to engine type and the working conditions they are able to cope with. This system grades engine duty without effecting the SAE viscosity classification.

The API engine oil service category[9] is defined in terms of these performance level; "**S**" for Service application (passenger car gasoline engines and light trucks) and "**C**" for commercial applications (heavy duty diesel engines). Some of the current service categories are listed below.

- **SM**: current category (November 2004) for all automotive engines currently in use. The SM oils are designed to provide improved oxidation resistance, improved deposit protection, better wear protection, as well as improved low-temperature performance over the life of the oil. Some SM oils may also meet the latest ILSAC specification and/or qualify as Energy Conserving.
- **SJ**: current category for 2001 and older automotive engines.
- **CI-4**: current category (October 2002) for high-speed, four-stroke engines designed to meet 2004 exhaust emission standards implemented in 2002 diesel engines. CI-4 oils are formulated to sustain engine durability where exhaust gas recirculation (EGR) is used and are intended for use with diesel fuels ranging in sulphur content up to 0.5% weight; can be used in place of CD, CE, CF-4, CG-4, and CH-4 oils. Some CI-4 oils may also qualify for the CI-4 PLUS designation.
- **CH-4**: current category introduced in 1998, for high-speed, four-stroke engines designed to meet 1998 exhaust emission standards. CH-4 oils are specifically compounded for use with diesel fuels ranging in sulphur content up to 0.5% weight; can be used in place of CD, CE, CF-4, and CG-4 oils.
- **CG-4**: Introduced in 1995, for severe duty, high-speed and four-stroke engines using fuel with less than 0.5% weight sulphur. CG-4 oils are required for engines meeting 1994 emission standards; can be used in place of CD, CE, and CF-4 oils.

Based on these categories, engine lubricant products that satisfy the most current requirements are licensed to display the API's Certification Mark "Starburst" and Service Symbol "Donut". These identify the lubricating oils suitable for gasoline and diesel engine vehicles[9].

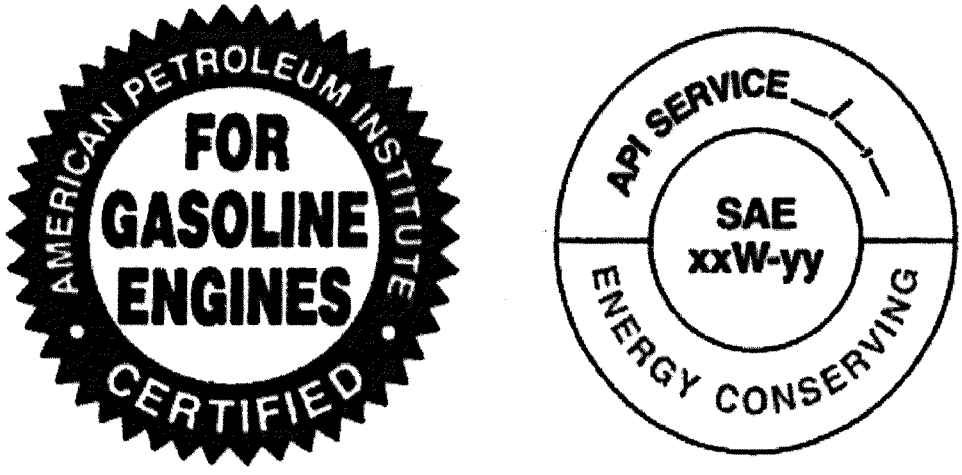


Figure 4a-b: The API certification mark and service symbol

The Certification Mark "Starburst" is designed to identify specific application of the engine oils (e.g. gasoline service).

The Service Symbol "Donut" is divided into three parts.

1. The upper part describes the oil's Service Category (e.g. SM or CH-4).
2. The centre identifies the oil's SAE viscosity grade (e.g. 5W-30).
3. The energy conserving notation is in the lower part.

The API classification system by definition meets the requirements of most vehicle industry around the world therefore many automobile manufacturers recommend lubricants that carry the API Certification Mark.

1.3 Lubricant Formulation

Formulating a lubricant is elaborate and time consuming. Lubricant formulations are mainly driven by vehicle manufacturer requirements, performance specifications, and consumer needs. Therefore the different aspects of oil performance requirements are considered concurrently in the formulation process.

Engine lubricants contain predominantly base oils usually up to 95% of the finished product (depending on performance level) and the remainder being additives (5-20%)[10]. Additives are included to improve the effectiveness of the base oil by imparting new performance characteristics to strengthen desired applications and help extend service life.

Although lubricants are formulated to meet product/performance requirements, it is also vital that the formulated oil can function as required during service use.

1.3.1 Base Oils

Base oils are the major working component of lubricants. Although it is possible to operate an engine on base oil alone, they are not sufficient for the operating conditions of modern engines.

There are two main types of base oils, natural base oils (mineral) and the synthetic base oils.

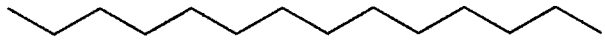
1.3.1.1 Mineral Base Oils

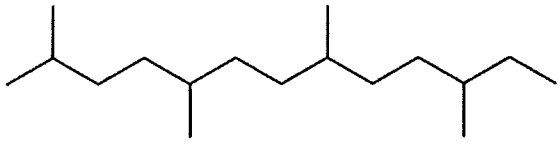
Mineral oils are selected hydrocarbon fractions derived from refined crude oil. Crude oil is a complex mixture of organic substances, mainly hydrocarbons and small amounts of other elements like oxygen, sulphur, nitrogen, phosphorus. The exact composition of a crude oil depends on its geographic provenance. The mineral oil fraction ranges from carbon atoms 14 to 40 in three hydrocarbon types. Different grades of mineral base oils are produced; their resulting performance characteristics are influenced by the selection and refining procedures.

The three main groups of hydrocarbons that characterise the mineral oils for lubrication functions are:

Aliphatic ('paraffinic') – general formula $C_nH_{2n+2,}$ are saturated hydrocarbons with linear or branched chain structure.

Linear- Alkanes

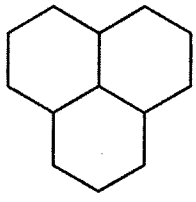




Branched-Alkanes

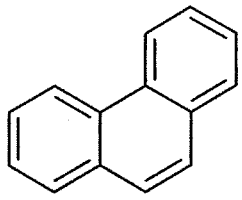
Paraffinic base oils are produced from crude oils that have relatively high alkane contents. They are preferentially used to formulate automotive lubricants required to meet current performance standards for lighter-viscosity motor oil formulations such as 5W-20 and 5W-30, as well as requirements for other lubricants[11]. Paraffinic oils have better oxidation stability, higher viscosity index and lower volatility relative to comparable viscosity grade naphthenic base oils. These types of crude petroleum are found in the North Sea, Middle East and some areas in the USA.

Alicyclics (Naphthenes) – are saturated cyclic hydrocarbons based on five and six member rings.



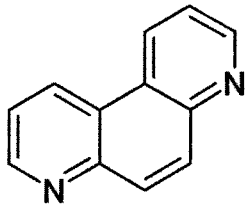
Naphthenic base oils are produced from a limited range of crude oils and in smaller quantities than paraffins. They have naturally lower pour points and superior solvency characteristics, compared to paraffinic base oils. Naphthenes are particularly useful in formulating low temperature, metal working oils and cylinder lubricants for large engines. These types of oils are commonly found in Nigeria and Venezuela.

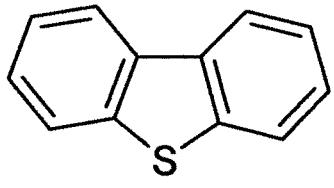
Aromatics – $C_{4n-2}H_{2n+2}$, cyclic structure hydrocarbons, mainly six-member/multiple ring structures based on the benzene ring, often with aliphatic/alicyclic side chains.



Aromatics have high densities and viscosity properties, they have good solvency power for additives but their stability to oxidation is rather poor.

Non-Hydrocarbons - The other elements found in crude oil are incorporated within ring structures, or as functional groups attached to an hydrocarbon. The heterocyclic structures often give anti-oxidant properties to the base oils.





1.3.1.2 Performance Properties of Mineral Oils

The Standard systems (IP and ASTM) have adopted some specification requirement tests to assess physical/chemical properties related to lubricating oils. Some of the most common properties required are discussed below.

Viscosity: is defined as the property of a fluid that measures its resistance to flow; liquids with low viscosity will flow more rapidly than a high viscosity liquid. Viscosity is an important property of a lubricant because it influences the ability of the oil to remain between moving surfaces, thereby minimising friction and reducing wear. Engine oil viscosity is commonly defined and tested using these four methods.

1. **Kinematic Viscosity**: measures the viscosity of an oil as it flows under the force of gravity. Measurements are taken at two temperatures representative of oil in the sump of a warm engine: 40° C and 100° C. ASTM D445 or IP 71 defines the measurement of kinematic viscosity.
2. **High-temperature High–shear-rate (HTHS)**: indicates the oil's resistance to flow in the narrow spaces between swiftly moving parts of a totally warmed up engine. The ASTM D4683 test simulates the conditions in an engine's crankshaft, connecting rod bearings and other narrow regions.
3. **Cold Cranking Simulator (CCS)**: this measure simulates the viscosity of an oil in crankshaft bearings during a cold start of the engine. The ASTM D5293 simulates an oil's cranking resistance when cold thus indicating the lowest temperature at which an engine is likely to start.
4. **Cold Pumpability**: measures the resistance of an oil to pump through the engine after a cold weather start. The ASTM D4684 (Mini-rotary viscometer method) test determines whether an engine runs with proper lubrication after the cold start.

Based on the above measures, the SAE created their viscosity classification standard (SAE J300)[8] for engine oil: The table shows the limits for each viscosity grade as discussed earlier in Section 1.2.

Table 1: SAE Viscosity Grades for Engine Oils — SAE J300 2004

SAE Viscosity Grade	Low Temperature Viscosities		High-Temperature Viscosities		
	Cranking (cP)[1] max @ temp °C	Pumping (cP) max with no yield stress @ temp °C	Low Shear Rate Kinematic (cSt)[2] @ 100°C		High Shear Rate (cP) @ 150°C min
			min	max	
0W	6200 at -35	60000 at -40	3.8	-	-
5W	6600 at -30	60000 at -35	3.8	-	-
10W	7000 at -25	60000 at -30	4.1	-	-
15W	7000 at -20	60000 at -25	5.6	-	-
20W	9500 at -15	60000 at -20	5.6	-	-
25W	13000 at -10	60000 at -15	9.3	-	-
20	-	-	5.6	< 9.3	2.6
30	-	-	9.3	< 12.5	2.9
40	-	-	12.5	< 16.3	2.9 (0W-40, 5W-40, 10W-40 grades)
40	-	-	12.5	< 16.3	3.7 (15W-40, 20W-40, 25W-40, 40 grades)
50	-	-	16.3	< 21.9	3.7
60	-	-	21.9	< 26.1	3.7

The "W" grade pertains to low-temperature performance while the non-W grades relates to high-temperature performance. The pumping and cranking limits for the W grade oil are specified, this is to ensure that if the oil allows the engine to start then oil will pump throughout the engine.

[1] 1 cP=10^{-3} N m^{-2} s

[2] 1 cSt=10^{-6} m^2 s^{-1}

Viscosity Index (VI): is used to indicate changes in the viscosity of a lubricant with varying temperature (i.e. the viscosity/temperature relationship). VI is calculated from kinematic viscosities taken at measured temperatures of 40°C and 100°C. If an oil sample has a low viscosity index, its viscosity would change rapidly with changes in temperature, but if VI is high then viscosity changes less with temperature. In practice high VI is used to formulate better-quality lubricants. It can be useful for machinery operating at a broad temperature range. ASTM D2270 or IP 226 defines measurement of viscosity index.

Pour Point: is a viscosity temperature phenomenon (increases with viscosity). It is defined as the lowest temperature at which a lubricant will flow by gravity alone; it is the last temperature before movement of the oil ceases. ASTM D97 or IP 15 relates to measurement of pour point; it describes the procedure for cooling oil until movement stops.

Cloud Point: is defined as the temperature at which a wax cloud first appears on cooling mineral oil under specified conditions. The cloud point is measured using ASTM D2500 or IP 219, which describes the procedure for cooling until the first sign of cloudiness, occurs.

Volatility: evaporation loss is particularly important to vehicle and cylinder lubrication because high temperature operating conditions increases the tendency of oil to be lost by vaporisation. Significant evaporative loss of oil leads to excessive oil consumption and destructive changes in oil properties. Volatility is measured by following ASTM D972 which determines the evaporation loss of lubricating oils at high temperature.

Flash Point: is defined as the lowest temperature at which the oil vapours will ignite, but not sustain a flame under specified conditions. Flash point is measured using ASTM D92 and D93. Flash point evidently relates to fire safety. It therefore used to assess the overall hazard of an oil and consequently used in transporting and safety regulations to define flammability of the lubricant.

Thermal Stability: this is the ability for an oil to endure high temperature operating conditions. It is vital that under this condition the oil does not decompose rapidly.

Chemical Stability: is the ability for an oil to resist chemical attack, which is assessed in relation to the surface, which the oil is expected to be in contact with. Lubricant oil is attacked chemically by oxygen from air, water and other combustion by-products that cause degradation of the oil's performance. The chemical stability of oil is related to thermal stability as chemical reactions increase with temperature increase.

The sulphur content of base oils is commonly regarded as an indicator of oxidation resistance, because the naturally occurring organosulphur compounds in crude oil are moderately effective in destroying peroxide intermediates and breaking down the oxidation chain mechanism.

1.3.1.3 Synthetic Base Oils (Chemically formulated)

As technology in industrial and automotive machinery developed, it became impossible to meet the more severe operating conditions using mineral base oils. To fulfil the increasing physical and chemical demands of developing engine technology, chemically formulated base fluids known as "synthetic base oils" were introduced. Synthetic in the lubricants industry has historically been synonymous with catalytic polymerized base oils such as poly-alpha olefins (PAOs). The term "synthetic" was specified by the industry because these types of oils were the only components available for high-performance lubricants at that time[12].

Current importance of synthetic lubricants follows environmental regulations issued by legislative bodies, which demand biodegradability, combined with non-toxic and recyclable characteristics. In addition vehicle manufacturers are requiring lubricants with longer service life and increased energy efficiency.

Synthetic base oils are found in all areas of lubrication due to advantageous properties such as:

- improved wear protection;
- longer service life;
- high temperature and oxidative stability;
- wider operating pressure and temperature range.

There are many useful compounds for the production of synthetic lubricants, however only about seven of them have significant industrial applications. The two major

chemically formulated base oils, **Synthethic Esters** and **Poly-Alpha-Olefins** generally used are discussed.

Synthetic Esters are made from condensation of acids and alcohols. Unlike mineral base oils, esters have uniform molecular structures and do not decompose at high temperature by means of free radical mechanisms. The major advantage of these types of base stock lies in their chemistry, which attracts them to metal surfaces giving them remarkable boundary lubrication and low temperature flow-ability.
Since these base oils are formulated chemically, it is possible to vary the design of the synthetic products to meet specification requirements. The main lubricant properties that are modified in this way include:

Viscosity - the viscosity of an ester lubricant may be altered in the following ways:

- enlarge the molecular weight of the carbon compounds by increasing the acid carbon chain or alcohol carbon chain or number of ester groups or degree of branching of the alkyl chains;
- introducing a cyclic group in the molecular structure.

Viscosity Index - the viscosity index (VI) of an ester lubricant can be increased by increasing the linearity, alcohol or acid chain length, and not using cyclic groups.

Pour Point - the pour point of ester lubricants is decreased by decreasing in the acid chain length and increasing the amount of branching. More interestingly, the position of the branch – a centre branch in the molecule gives a better pour point than branches towards the end, thus decreasing the internal symmetry of the molecule gives decreased pour points.

Thermal stability - The ester base oils are more stable than the mineral base oils. This leads to higher levels of cleanliness and reduces deposits in an engine.

Biodegradability - esters are relatively biodegradable, the initial and final products of ester base stocks are produced from generally acceptable non-toxic natural occurring acids and alcohols. Some ester base oils can be formulated to either respond or be resistant in order to meet biodegradability requirements as those defined by the

European Union and the (US) EPA. The direct effect of the ester group on the physical properties of a lubricant is due to strong dipole moments binding the lubricant together. The high-temperature performance of these fluids and their very low pour points are ideal for the wide temperature ranges encountered in today's operating engine conditions.

Poly-Alpha-Olefins (PAOs) - PAOs are made from hydrogenated oligomers of usually α-dodecene (C_{12} olefin). The first commercially feasible process for making PAO was pioneered by Gulf Oil in 1951 using an $AlCl_3$ catalyst. Mobil patented and improved the process using a $BF_3/AlCl_3$ catalyst in the 1960s and first used it in specialty products such as Mobilgrease28, which solved a wheel bearing failure problem on aircraft carriers in cold climates[13]. PAOs became major lubricant components when Mobil Oil began marketing their product.

PAO's are said to be the 'ideal paraffinic lubricants' but the cost of achieving this is very substantial compared to conventional oils. Following its introduction, the PAO market developed slowly with steady growth due to higher cost. However in the last 10 years, the PAO market significantly increased, first in Europe and then in North America. The growth may be attributed to the stricter lubricant specifications in Europe that created a market place for synthetics and semi-synthetic products[12]. The Properties of PAO's include:

- a wide temperature performance range;
- low pour points and volatilities;
- good viscosity;
- oxidative stability;
- good additive solubility.

Due to their structure, PAO have inherent high viscosity index and resistance to shear which allows the formulation of wide temperature range and multigrade lubricants with little need for VI additives.

The ability to control the compositions of the PAO's simplifies the formulation of high quality lubricants. PAO's are used in both fully synthetic and semi-synthetic automotive lubricants.

1.3.1.4 Semi-Synthetic Lubricants

Semi-synthetic is a term that indicates that the oil is a blend of synthetic and mineral-based oils (plus additives). They are designed to provide the benefits of the oxidative stability, high-temperature performance and other excellent lubricating properties of synthetic oils without forfeiting the natural solvency provided by mineral oil and matching the cost of pure synthetic oil.

1.3.1.5 Classification of Base Oils

The API (1990) established base oil classification system to help marketers to minimise re-testing costs, when blending licensed engine oil with base oils from different refineries. The system used physical and chemical parameters to divide all base oils into the following five groups listed in the table below:

Table 2: The API - Classification of Base Oils[14]

Group	Saturate wt %	Sulphur wt %	Viscosity Index
I	<90	> 0.03	> 80 to < 120
II	≥ 90	≤ 0.03	≥ 80 to ≤ 120
III	≥ 90	≤ 0.03	≥ 120
IV	All poly alpha olefins (PAOs)		
V	All base stocks not included in Groups I-IV		

Group I - these base oils are the least refined (solvent freezing) of all the groups. They are usually a mix of different hydrocarbon chains with good volatility property.

Group II - produced by hydro-processing and refining, are commonly used in mineral base oil. automotive engine oil. They offer relatively good lubricant performance properties such as oxidative stability, volatility and flash point.

Group III - produced from the utmost level of hydro processing and refining available for mineral oil development. They are marketed as synthetic or semi-synthetic products due to their capability of good performance in wide range conditions. This fluid is commonly mixed with additives.

Group IV - produced by chemical reactions. They are chemically engineered synthetic base stocks. When combined with additives they provide high-quality performance properties. They have very stable chemical composition due to uniform molecular chains. They are more common in synthetic blend products for automotive and industrial applications.

Group V - are base oils used primarily for developing oil additives that add beneficial properties to other base oils. Esters and polyol-esters are common examples of group V base oils.

1.3.2 Lubricant Additives

Additives are used extensively today, with applications ranging from automotive to several other industrial uses. Additives are added to the lubricating oils in order to prolong the life and to enhance the performance properties of the oil.

These additives offer a broad range of qualities essential to enhance the performance characteristics of mineral, semi-synthetic, and synthetic base oils. Subsequently the base oil functions as a solvent for the additives.

Applications that place more demand on lubricants need better additives, possibly in larger amounts than good quality base oils. Additives can influence each other as well as the lubricant both antagonistically and synergistically.

Lubricant additives are classified based on their functionality, which fall into the following categories below.

Additives which modify base oil properties to meet formulation requirements.

Additives which protect base oil in formulations through the use of anti-oxidants which inhibit oxidative degradation of the base oils.

Additives which protect the internal surface of the engine from the combustion process and chemical deposits.

Additives which clean the engine keeping the system free of particulate deposits and prevent the agglomeration of particles which may block oil delivery lines.

1.3.2.1 Base Oil Modifiers

Viscosity Index Improvers (VII's): These types of additive modify the viscometric properties of the base oils to give lower viscosity at low temperature and also higher viscosity at higher temperature. They are long chain polymers that are relatively stable to shear degradation, cost effective and non-toxic. The most common examples are polymethacrylates (PMA's).

Pour Point Depressants: The pour point depressants are used to prevent problems with poor oil pumpability due to congelation. At low temperatures some lubricating oils solidify with large crystals which can block oil ways and restrict the flow of oil in an engine. The pour point depressant is used to improve the low temperature properties; they inhibit the formation of large wax crystals and maintain the flow of oil in an engine. Examples are polymethracrylates and polyacrylates.

Friction Modifiers: These are used to reduce the coefficient of friction between engine surfaces. The addition of friction modifiers to the crankcase lubricants was shown to significantly reduce the mechanical losses of critical components within the internal combustion engine thereby improving fuel economy[15].

1.3.2.2 Base Oil Protector

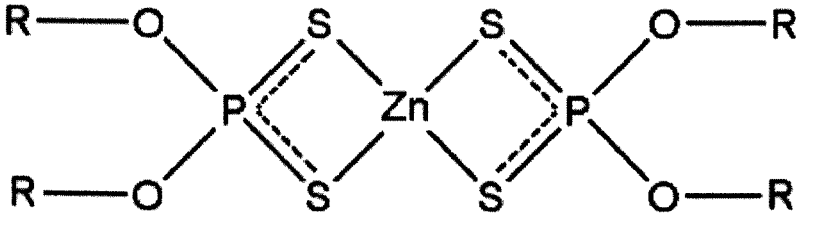
Antifoam agent: Due to high shear rates of engine components, emulsions and foam develop. Foams weaken the effect of lubrication by blocking oil pathways and prevent adequate supply of oil around the engine. The main antifoam chemicals used are polydimethylsiloxanes for non-aqueous foams.

Antioxidants: Lubricants are usually susceptible to oxidation when used. Even during the refinery process lubricants lose their natural antioxidants. The oxidation results in the formation of unwanted peroxides and acids. Antioxidants are added to prevent the formation of these corrosive products and help maintain oil performance. Zinc dialkyldithiophosphates (ZDDP's), aromatic amines and hindered phenols are the main antioxidants used.

1.3.2.3 Engine Protector

Corrosion Inhibitors: prevent corrosion by creating a physical barrier in form of a hydrophobic, monolayer of chemisorbed surfactant molecules on the metal surface, which prevents access of water and oxygen to the metal surface. Examples are phosphate esters and sulphonates.

Anti-Wear Additives: ZDDP's reduce wear by forming thick glass-like boundary lubrication films between 100-200° C. The ZDDP's have multi-functional properties such as anti-oxidant, corrosion inhibitors as well as anti-wear properties.



The main compounds used in industrial and automotive applications are the metal-phosphorus-sulphur compounds such as the ZDDP's which are also used as antioxidants.

1.3.2.4 Engine Cleaning Additive

These additives have a direct effect in prolonging engine life[16]. They promote appropriate oil flow properties by minimising oil thickening and the formation of carbon sludge that clogs oil pathways in the engine. Without these additives there is loss of oil control, a resultant effect of ring sticking due to deposits on the piston ring and grooves. Loss of oil control is described as:

- increased oil flow upward into the combustion chamber, which burns during engine combustion thus leads to increased engine exhaust emissions;
- incomplete combustion leads to deposits that cause valves to stick;
- increases oil consumption (i.e. more oil required between drain intervals);
- reduces the life of the oil through contaminated combustion gases which flow downward between the cylinder liner and piston rings into the oil crankcase.

Detergents: The detergent molecules are made up of polar head containing a metal cation (Ca^{2+}, Mg^{2+} or Na^{+}) attached to an oleophilic group hydrocarbon tail.

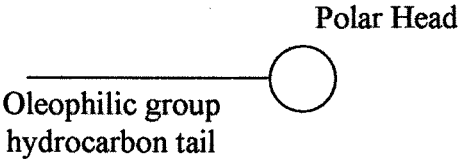


Figure 5: Detergent polar substrate

The hydrocarbon tail acts as a solubilizer that enables the detergent to be completely soluble in the base oil. The head is attracted to polar contaminants in the lubricant. Engine oil detergents enhance the alkaline reserve of lubricants, which neutralise organic and inorganic acids such as nitro acids, sulphur acids and oxy acids formed during the fuel combustion process.

There are four major types of detergent polar substrate: sulphonates, phenates, salicylates and phosphonates. Use of salicylates is limited while that of phosphonates is minimal.

Sulphonates

The sulphonates are the most widely used detergent additives. They provide higher antirust properties and neutralise acidic components in the oil. Two types of sulphonate detergent exist: petroleum or natural sulphonates and synthetic sulphonates.

1. **Petroleum sulphonates** are metal salts formed as by-products in the manufacture of white oils which involves sulphuric acid treatment of mineral oil. The quality performance of the resultant sulphonate is predominantly dependent on the source and type of base oil used in the white oil production. Paraffinic base oils are reportedly[17] very much preferred to naphthenic base oils. Sulphonates derived from the paraffinic base oil are resistance to oxidation, as the naphthenic are found to be more corrosie to copper-lead bearings.
2. **Synthetic sulphonates** are metal salts specifically produced from a synthesized alkyl or aromatic substrate. Usually synthetic sulphonates are derivatives of benzene with long alkyl substituents, some of which are used for the production of oil soluble sulphonates.

There are two general types of natural and synthetic sulphonates namely neutral and overbased sulphonates.

Neutral sulphonates are produced by the reaction of a sulphonic acid with either metal oxide or metal hydroxide.

$$RSO_3H + \begin{matrix} MO \\ or \\ M\text{-}OH \end{matrix} \longrightarrow RSO_3M + H_2O$$

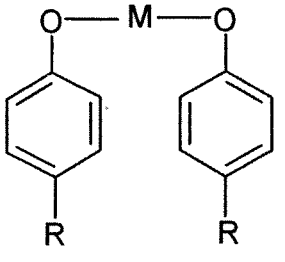
Overbased sulphonates are produced by the reaction of neutral metal sulphonates and metal hydroxide. The term 'overbased' means that the sulphonate contains metal in excess of the stoichiometric amount required to produce a neutral one.

$$RSO_3M \quad xM\text{-}OH \xrightarrow{CO_2} RSO_3M{-}{-}xMCO_3 + H_2O$$

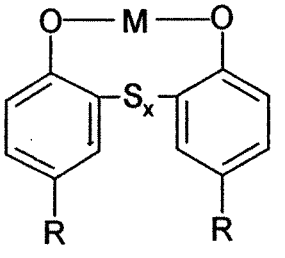
This complex reaction is carried out using carbon dioxide in the presence of an alcoholic material promoter. The promoter dissolves some of the metal hydroxide which reacts with the CO_2 to form a metal carbonate. These types of sulphonates are very good at neutralising acid components.

Phenates

The phenates are particularly important for acid neutralisation; they are useful for high temperature detergency and oxidation inhibitors. Metal phenate includes salts of alkylphenols, alkylphenol sulphides and alkylphenol-aldehyde condensation products.



Normal Phenate



Phenate Sulphide

Calcium and magnesium metal phenates are currently the most widely used in engine lubricants. Basic phenates, having higher acid neutralisation potential, are formed by use of excess metal base over the theoretical required amount to form normal phenates.

Dispersants: In the 1950s a new type of non-metallic ashless dispersant additive was introduced, as previous engine cleaning agents (sulphonates, salicylates and phenates) were not compatible with low temperature and short distance driving.

This product known as succinimide dispersant has a similar structure to that of the detergent. A hydrocarbon tail (oleophilic group), usually of higher molecular weight than those of the detergents, is attached to a polar head group containing one or more of the elements oxygen, nitrogen, sulphur, and phosphorus. These additives are categorised mainly into:

- high molecular weight polymeric dispersants used in multigrade oil formulation;
- lower molecular weight additive used where viscosity modifiers are not required.

This dispersant function by attaching the polar heads to the sludge formed in the oil. The dispersant traps sludge in its core (micelle) and keep it in suspension until the engine oil is drained finally.

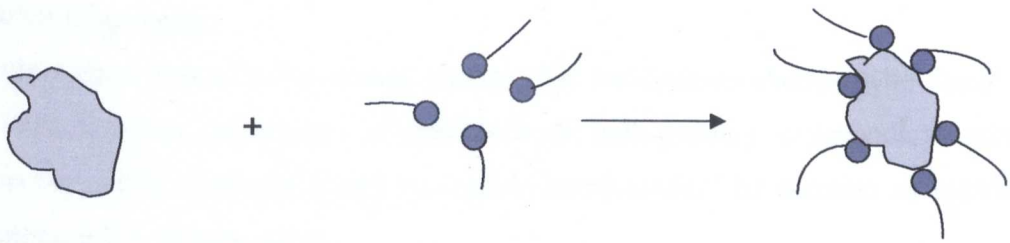


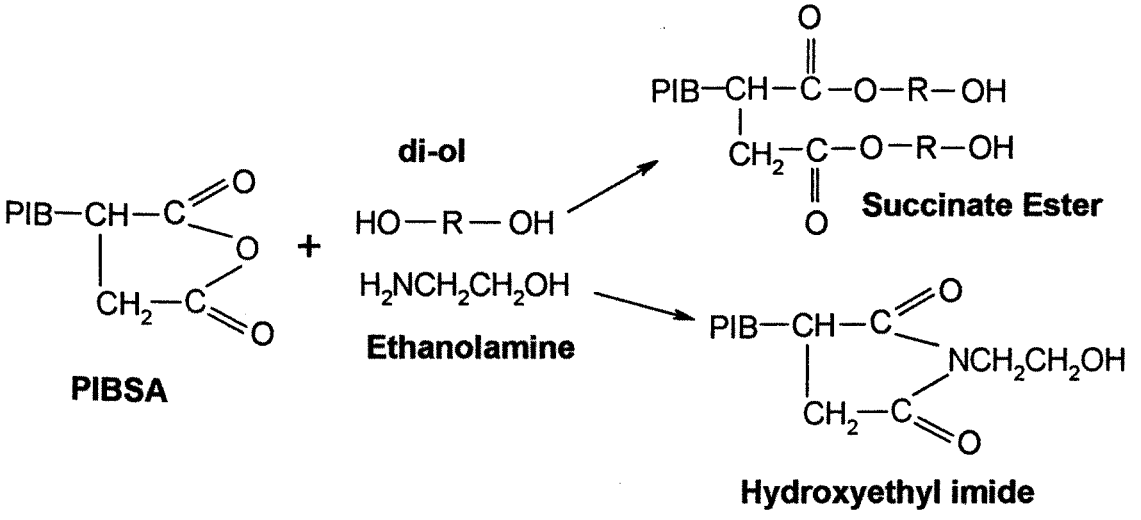
Figure 6: Interaction of the dispersant's polar heads with sludge

Most dispersant currently used in engine oils are prepared from polyisobutylenes of 1000 to 10000 relative molar mass, with either phenolic or succinic acid groups that provide the polar functionality.

There are four different types of dispersants; products with succinic acid groups (1) succinimides, (2) succinate esters, and products from phenols (3) alkyl hydroxybenzyl polyamines (known as Mannich dispersants) and (4) phosphorus compounds.

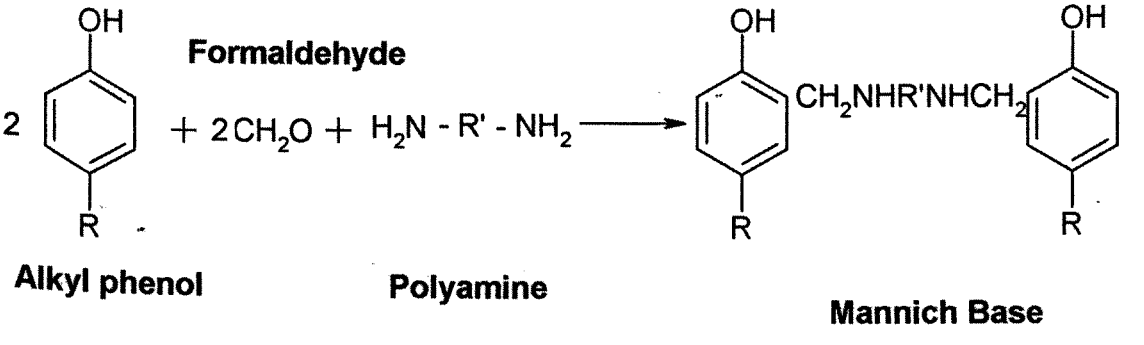
Succinimides and Succinate Esters

The succinimides and succinate esters are currently the materials of commercial importance. They are both derived from the same chemical intermediate Polyisobutenyl Succinic Anhydride "PIBSA".



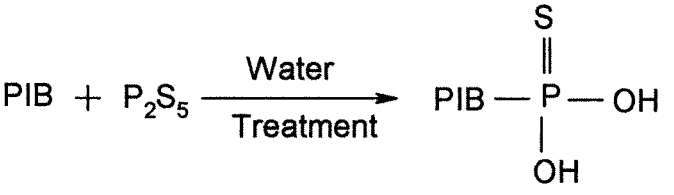
Mannich Dispersant

The often called Mannich dispersant, named after the German chemist who discovered it in 1912, involves the reaction of formaldehyde with primary or secondary amine to replace the active hydrogen atoms in organic compounds. The reaction as applied to lubricating oils is shown below.

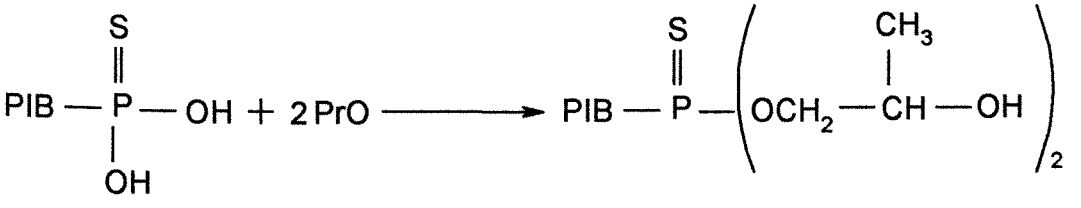


Phosphorus Dispersant

Phosphorus is incorporated into dispersants by a two-step reaction, polyisobutylene (PIB) is first reacted with phosphorus pentasulphide under high temperature conditions



The resulting mixture is then treated with water to remove sulphur and form phosphorus acid which is finally treated with propylene oxide to form the hydroxypropyl esters of the phosphorus acid.



To provide optimal performance more than one of these dispersants is used in engine oil formulation. The distinctive structural property of the detergents and dispersants give them their ability to act as cleaning agents that prevent carbon and sludge deposits in the engines.

1.4 Lubrication of the Internal Combustion Engine

The engine is the heart of a car and keeping it lubricated helps the engine run better and last longer. The engine lubrication system is designed to deliver clean oil at the right temperature and pressure to every moving part of the engine.

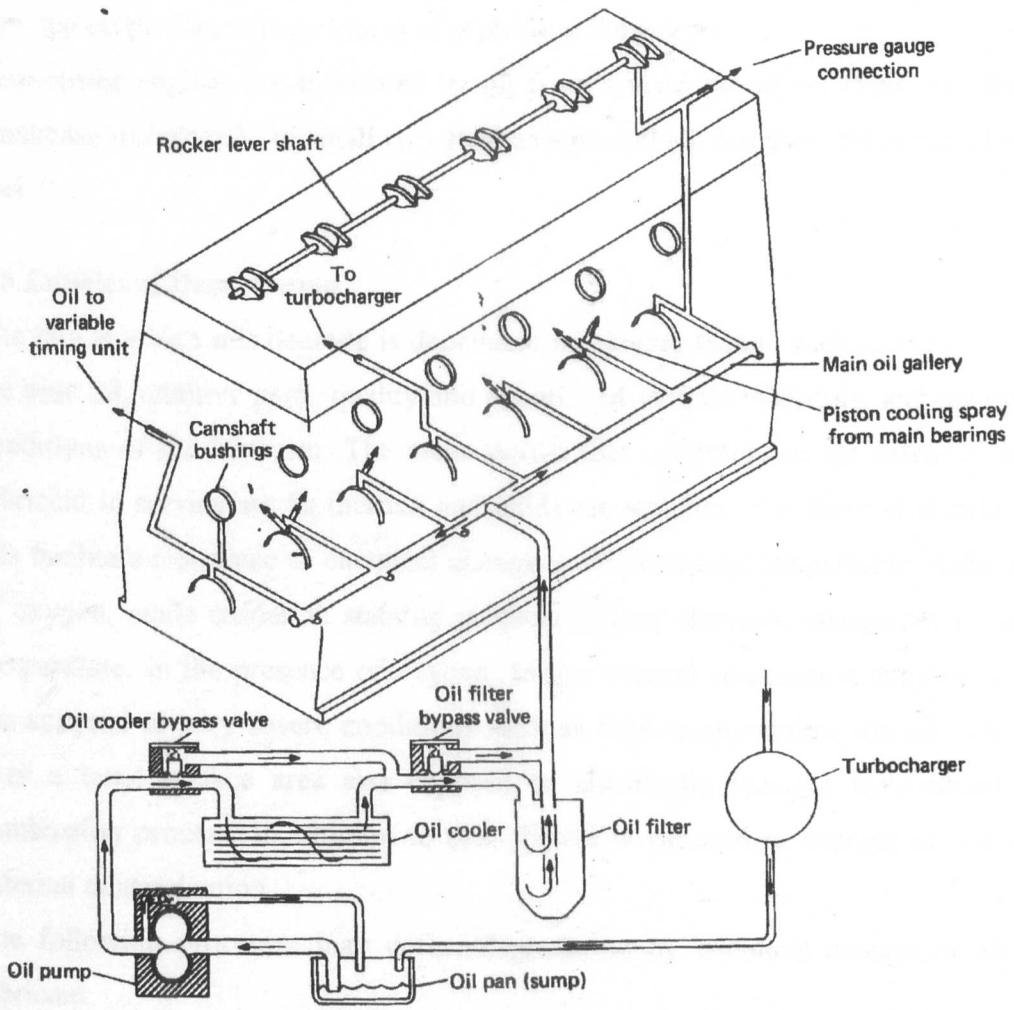


Figure 7: Diagram illustrates lubricating oil flow through the Engine[18]

The oil reduces metal-to-metal friction by forming a thin, slippery film on surface of the metal parts of the engine. The two major areas that require lubrication are the pistons for easy sliding in their cylinders and bearings that allow the crankshafts and camshafts to rotate freely.

The oil is sucked from the oil sump by the pump. It then passes through the oil filters and is pressure fed into the bearings. A gauge measures oil pressure. From the main bearings, the oil passes through feedholes into drilled passages in the crankshaft and on to the big-end bearings of the connecting rod. The cylinder walls and piston-pin (little-end) bearings are lubricated by oil fling dispersed by the rotating crankshaft. The excess oil drips back into the sump where the cycle begins again. This constant circulation is how the oil performs its functions of protecting the engine.

Four-stroke engines are lubricated by oil from a separate oil reservoir, usually in the crankcase underneath. In small two-stroke engines the lubricating oil is mixed with the fuel.

1.5 Lubricant Degradation

The rate at which oils degrade is dependent on several factors such as the chemistry of the base oil, additive pack, quality and quantity of various inhibitors, and the operating conditions of the lubricant. The main factors that contribute to the extended life of a lubricant in service are its thermal and oxidative stability. The thermal stability of the oils facilitate resistance to chemical change with increasing temperature in the absence of oxygen, while oxidation stability protects against chemical change with increasing temperature, in the presence of oxygen. In the internal combustion engines lubricants are exposed to very severe conditions such as high temperatures; the oil is dispersed over a large surface area and exposed to chemically reactive by-products of the combustion process. In addition to this, the oil is exposed to sources of internal and external contamination.

The following processes may define degradation by chemical change of an engine lubricant:

1.5.1 Oxidative Degradation

At the elevated temperatures of an operating engine oil that is exposed to oxygen can be oxidized to form carbonyl (C=O) compounds such as esters, ketones and carboxylic acids. The oil dissolves some of these compounds, while some remain suspended due to dispersive additives in the oil. The effect of prolonged oxidation is that, chemically the oil becomes acidic causing corrosion, and increase in viscosity.

The reaction mechanisms that describe the oxidative degradation of engine lubricants at two operative conditions are described below.

1.5.1.1 Oxidation at Low Temperature

The degradation of oil at relatively low temperatures in an operating engine occurs by a free radical mechanism. The reactions take place in the following four stages:

Initiation of a radical chain: under normal conditions this process is catalysed by traces of transition metal ions to produce alkyl radicals such as R (CH_3) CH·

Propagation of the radical chain: the alkyl radical produced from the previous stage reacts irreversibly with oxygen to form alkyl peroxy radicals of the form R (CH_3)CH — OO·

The rate of the reaction is dependent on the type of substituents attached to the carbon atom for example a tertiary alkyl radical reacts 10 times faster with oxygen than a methyl radical.

The subsequent step in this reaction is the formation of hydroperoxide and alkyl radicals. This occurs by abstraction of a hydrogen atom by a peroxy radical from another hydrocarbon:

$$R(CH_3)CHO_2^{\cdot} + R'H \longrightarrow R(CH_3)CHO_2H + R'^{\cdot}$$

Chain branching: the various types of hydroperoxides produced during the early stages of autoxidation, at low concentrations form alkoxy and hydroxyl radicals.

Due to high activation energy this reaction is thwarted and only significant under catalysed or at higher temperatures conditions. The hydroxy and primary alkoxy radicals formed are very active; they can abstract hydrogen atoms in non- selective reactions. The secondary and tertiary alkoxy radicals form aldehydes and ketones:

Termination of the radical chain reaction: is the final phase of the oxidation process; autoxidation then autoretardation before the hydrocarbon is completely used and the oxidation process stops. However termination may be affected by the combination of peroxy radicals to form unreactive ketones and alcohols.

1.5.1.2 Oxidation at High Temperature[19]

At elevated temperatures, >120°C the degradation process is divided into a primary and a secondary phase. The chart below illustrates this process:

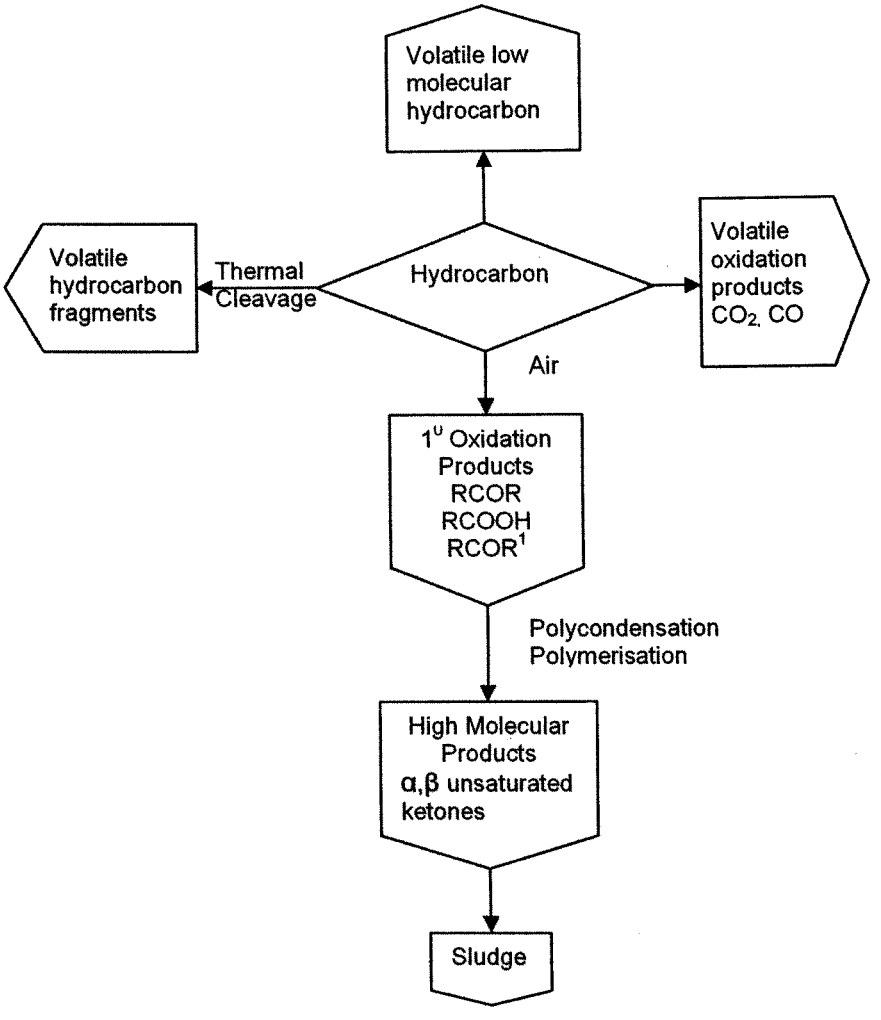


Figure 8: A model of oil degradation process under high temperature conditions

Primary Oxidation phase: The initial steps involved in this process are similar to the radical mechanism under low temperature conditions. However the cleavage of hydroperoxides at high temperatures is vital, but the selectivity is reduced and the reaction rate is increased. Some of the major products from this oxidation conditions are carboxylic acids (RCOOH) and ketones (RCOR). Carboxylic acids contribute to the acidity of the oil which depletes the alkaline reserve of the oil through neutralisation.

Secondary oxidation phase: the viscosity of the medium increases due to polycondensation of the difunctional oxygenated products (ketones) formed in the primary phase. Further polycondensation (via acid or base catalysed aldol condensation reactions) yield high molecular weight intermediates products known as sludge.

The total effect of prolonged oxidation causes corrosion of the engine parts due to an increased level of acid in the oil.

1.5.2 Combustion Products[20]

Nitration Products-nitration products are formed when organic components present in the oil are exposed to high temperatures and pressures in the presence of nitrogen and oxygen. The products formed are generally nitro-oxides such as NO, NO_2, and RNO_3. These nitro products are the major cause of oil thickening and build-up of varnish or lacquer commonly found on the pistons, cylinder walls and combustion chamber

Sulphate Formation - sulphur compounds are commonly found in crude oils and in some additives used in formulation. They subsequently escape into the piston rings, seals, and build-up over time. Sulphur products such as SO_2 and SO_3 are formed by oxidation of these sulphur compounds. They also react with water formed during combustion to form strong inorganic acids such as H_2SO_4 which are neutralised by and therefore deplete the alkaline reserve of the additive package of the oil. These products increase the production of varnish and sludge and generally degrade the oil.

Water Contamination- water can come from sources within the engine such as the coolant system, combustion process or condensation (cold engine), or from reaction between additive packages.

Soot contamination- (carbon residue) soot particles are hydrocarbon fragments naturally found in diesel engine oils. They are produced from incomplete combustion of fuel. The lubrication properties of an oil deteriorates with high soot content leading to changes in the oil viscosity and blockage of oil filters. It is also indicative of combustion problems.

1.6 Lubricant Oil Analysis

Oil analysis involves sampling followed by measurement of various properties that indicate wear in an engine system and contamination of the lubricant. Regular sampling and analysis help establish a baseline of normal wear and can indicate when abnormal wear or contamination is occurring. By identifying and measuring these impurities, the rate of wear and level of contamination can be dertemined.

The techniques for assessing lubricating oil performance and condition are through laboratory, engine and field tests. These assesment provide awareness about:

- contamination in the oil;
- additive depletion;
- and general degradatioin condition of oil.

Early detection using oil analysis programme can prevent major failures and increase machine life. These methods are also useful for developing models, which support the functions of the lubricant such as in reducing wear and lower contamination levels.

The complexity of lubricant formulation and testing procedures in practice are elaborate and expensive. The ability to incorporate more and more aspects of the physical behaviour of lubricants into analytical modelling is an important and a fast developing field[21]. Predictive maintenance and condition monitoring are a necessity for industries, which are critical in achieving a production objective; as a result a systemic structured approach to economically feasible techniques for oil analysis was the prime goal of this work.

Chapter 2

Equipment, Experimental Material and Methods

2.1 Lubricant Performance Testing Equipment

Due to modern technology and the ever-increasing demands for higher performance engine lubricants, manufacturers persistently attempt to find a simpler and more cost effective formulation and test methods.

This chapter introduces the testing procedures associated with this research and the background to the experimental measurements performed during this work.

2.1.1 Engine Testing

There are numerous activities with considerably varying conditions which take place within an operating engine. For example lubricants are required to perform adequately under the rigour of an operating engine from the relatively cool conditions prevailing in the crankcase to the high temperatures of the piston crowns and valve system, whilst acting as coolant to the underneath of the pistons. During these processes, the lubricant is subjected to oxidation, exposed to other combustion by-products different metals which may have catalytic effects and. As a result no single laboratory test could simulate the conditions that characterise an engine; and assess the performance requirement of the lubricant. Therefore the most appropriate method of evaluating how an oil would perform is by implementing an engine test. However there must be a rationale and strategy for carrying out an engine test. These procedures are commonly designed to assess or rate the lubricants based on several prime considerations. To rationalise and standardise test methods, the ASTM and IP have clearly defined protocol for use through out the industry.

These methods are usually followed as a guideline. They can be modified to develop in-house testing methods or for research studies. An adaptation of such standard engine test method facilitated the study of degradation of lubricating oils in the Piston Ring zone of spark ignition engines by means of an "**internal oil drain sampling system**" at De Montfort University. The development was based on the concept that lubricating oil is vital to the piston of an engine and rapid degradation occurs in this area.

Engine pistons and their rings are amongst the most important components in the automotive field. The principal role of the piston ring pack is to:

- ❖ maintain an effective gas seal between the combustion chamber and the crankcase;
- ❖ transfer heat from the piston into the cylinder wall and then to the coolant;
- ❖ limit the amount of oil transported from the crankcase to the combustion chamber.

However the piston ring pack is also one of the largest sources of friction in the internal combustion engine. Analyses of samples taken from the piston region of internal combustion engines have shown that significant degradation of the lubricant occurs in this area[22-26]. Its close proximity to the combustion chamber makes it an extremely severe region, due to high temperatures, pressures and contribution from combustion by-products. The lubricating oil in this area is subjected to rigorous physical stress due to these conditions.

2.1.2 Petter AA-1 Sampling System

The internal drain sampling system developed by Simon Cupples[23] made it possible to obtain oil samples continuously from the piston ring zone during engine operation. The method was developed on a Petter AA-1 single cylinder diesel engine; a small industrial engine with capacity of 219 cm^3, compression ratio of 17:1 and maximum power output of 2.6 kW at 3600 rpm.

The idea of the internal drain system, indicated in Figure 9, was such that the oil sample was transferred via tubing from an orifice drilled behind the piston ring down the connecting rod and outside the crankcase to the collection point. This tubing provided a chemically inert environment that prevents further degradation of the oil sample.

A stepwise sequence of modifications to the piston, crankcase and connecting rod of the Petter AA-1 engine facilitated continuous sampling from several positions in the piston ring zone. Details of these adaptations and the procedures can be found in the PhD thesis of Simon Cupples (1992)[23]. Some of the data obtained from the Petter AA-1 experiments are reported in this thesis; the dataset was explored using some of the chemometric techniques described in Chapter 3.

The purpose of this analysis was to gain an insight into the performance of the lubricants in the piston ring zone region of the engine. The diagram below illustrates the oil sampling methodology with the internal drain system.

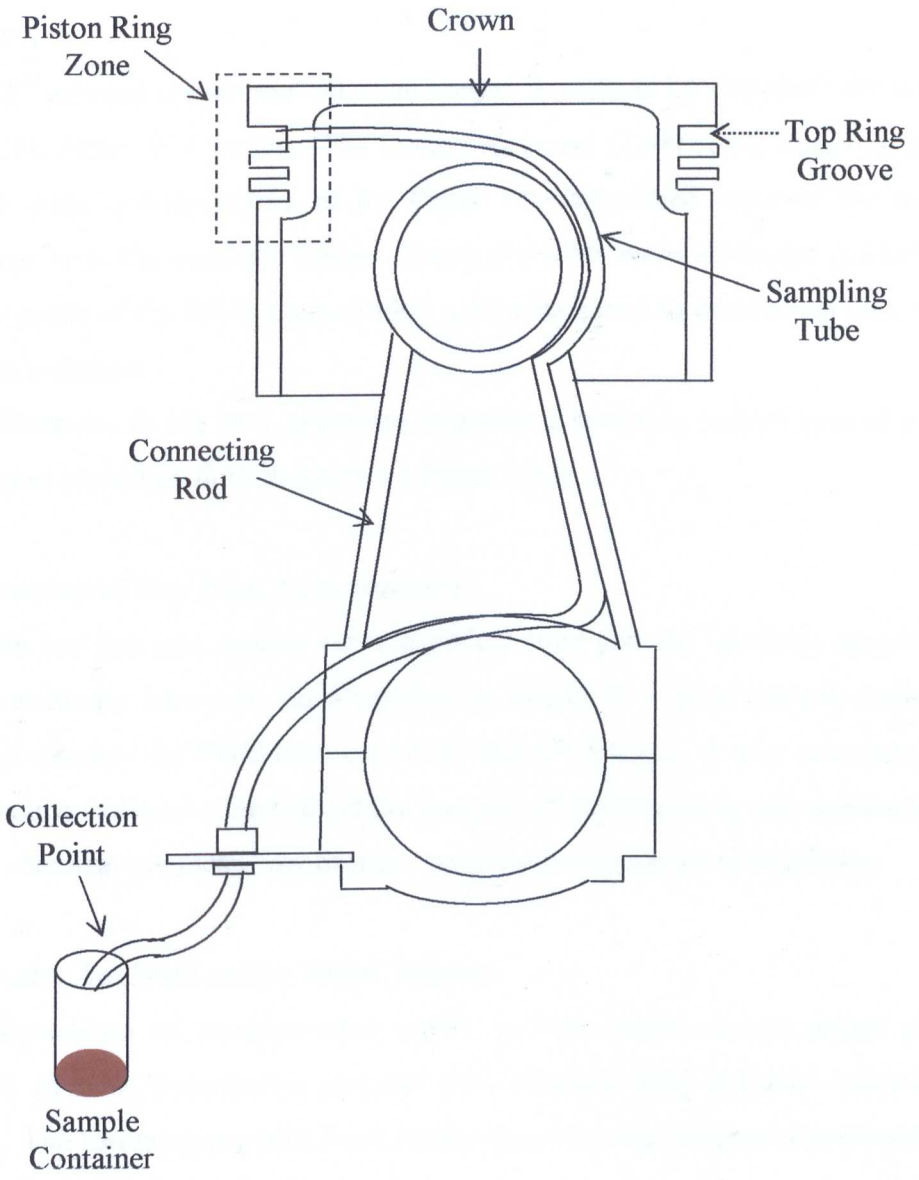


Figure 9: A schematic diagram of the internal sampling system used in the Petter engines

2.1.3 Petter W- 1 Sampling System

The Petter W-1 is a single cylinder, four-stroke spark ignition engine with side valves that has been adopted as a test engine by the Institute of Petroleum (IP). This engine is used to assess the degree of oxidation stability of oils, bearing corrosion tendencies and piston deposits. This engine is currently used as a standard IP lubricant test engine, Method IP 176/64[27].

Thompson[24] adapted the internal oil drain system developed by Cupples[23] for the Petter AA-1 to the Petter W-1 engine. The lower test speed (1500 rpm), compression ratio (5:1) and spark ignition nature of the Petter W-1 simplified some of the problems encountered with the previous engine. These problems were attributed particularly to the higher speed of the AA-1 engine (3000 rpm) which lead to mechanical failure of the tubing due to fatigue.

The modifications to the W-1 engine to establish a sampling system proved to be an improvement on earlier work done on the Petter AA-1.

2.1.4 Collection of Top Ring Zone Samples

The engine test run was usually for a specified time and the lubricant samples were collected at hourly intervals. As illustrated in Figure 9, a glass sample container is placed at the end of the PTFE tubing used for sample delivery. A new container is used for each hourly collection throughout the test period. PTFE tubing was commonly used due to its chemical inertness, low friction, and extreme temperature capability.

2.1.5 Samples Analysed on the Petter Engines

Several formulated oil samples were tested on both Petter engines under specified conditions. In some experiments samples were obtained from different regions of the ring zone. The formulations with brief details about the experimental conditions of the ring zone datasets are given below.

Petter AA-1 Test

BP Oil Technology Centre, Sunbury, supplied four fully formulated lubricants. The first three were formulated as a series of bridged combination lubricants of increasing quality.

1. Lubricant A – SAE 10W-30 oil, formulated with group I (mineral) base oil and additive pack 1 (formulated to give average performance).
2. Lubricant B – SAE 10W-30 oil, formulated with group I base oil and additive pack 2 (formulated to give better performance).
3. Lubricant C – SAE 5W-30 oil, formulated with group II (semi-synthetic) base oil and additive pack 2.
4. Lubricant D - 'Cummins Blue' SAE 15W-40 oil (a formulation for commercial US diesel trucks which extends their viscosity range.

These oils were sampled at two positions on the engine piston. The engine operated at a design load of 2.25 kW at 3000rpm, air-cooled for 10 hours. The used oil samples were collected every hour. More details can be found in Cupples's PhD thesis (1992)[23].

Petter W-1 Test

Three fully formulated lubricants samples were supplied by BP Oil Technology Centre Sunbury formulated and tested as a series:

- Good Lubricant - formulated to **'Pass'** the ASTM Sequence IIIE/VG tests;
- Borderline Lubricant - formulated tested to give **'Borderline'** result on the ASTM Sequence IIIE/VG tests;
- Poor Lubricant – formulated to **'Fail'** the ASTM Sequence IIIE/VG tests.

The engine operated at a design load of 2.5 kw at 1500 rpm, glycol cooled. The test period lasted twenty-four hours under the IP 176 test conditions[27] and samples were collected hourly. More details of this experiment can be found in the PhD thesis[26] of Asif Datoo (2003).

2.2 Condition Monitoring Technique

The concept of this approach was to collect and examine lubricating oil samples during service use. As described in Chapter 1 this procedure improves understanding of the chemistry of how lubricants perform when in service. By monitoring the progress of chemical degradation, the performance of the oil can be assessed. As part of this work field samples were obtained in the following ways:

- Over hundred used oil samples were collected from various vehicles. Samples of new oils, believed to have gone into these cars were also acquired from the different car dealership garages.
- Sequence sets; samples were collected approximately monthly to monitor the ageing and degradation processes of the lubricant. The two types of vehicles used were; Peugeot 1.9 diesel engine in Peugeot 306D and Honda 1.8 petrol engine in Rover 618iS.
- Supplied Castrol oils; diesel engine vehicle sump samples collected at timed intervals after 0 to 400 hours operation.

2.2.1 Collection of Sample from Vehicles

It was intended that a wide range of samples would be obtained from a larger number of vehicles types that had been used for diverse applications by drivers with quite different styles. Samples were taken from the sump of the car engine via the dipstick tube. The used oil was then transferred into a capped glass container for storage and transporting to the laboratory. A sampling kit was designed, which comprised:

1. A collection form that was designed to record and store details of the engine, type of oil, oil mileage and car mileage;
2. 20 mL syringe attached to 60-66 cm of nylon tubing. From experience this length was appropriate for most engines which had extended dip-stick tubes;
3. protection gloves, cleaning cloth and disposable bags for the used tubes and syringes.

Some oil samples were taken by the author, some by the vehicle owners and some by service garage personnel.

2.3 Analytical Equipment for Testing

This section describes details of the laboratory test procedures carried out on the lubricant samples. Details about the analytical instrumentation are given, as well as modifications made to some of the equipment.

2.3.1 Infrared Spectroscopy Analysis

Infrared spectroscopy or frequently Fourier Transform Infrared Spectroscopy is one of the most powerful techniques accessible to chemists. Its application is valuable for both research and routine studies, particularly for identification of compounds, characterising polymers, fingerprinting organic compounds and monitoring functional groups. Fundamentally it is an instrument that measures the relative radiation intensity against reciprocal wavelength in the infrared region.

The spectral region is classified into 'Far infrared' (4 – 400 cm^{-1}), 'Mid infrared' (400 – 4000 cm^{-1}) and 'Near infrared' (4000 – 14000 cm^{-1}). It can be applied to analysis of solid, liquid and gas samples. No two compounds have the same infrared spectrum.

2.3.1.1 Principles of Infrared Spectroscopy

When a molecule is exposed to infrared radiation, it absorbs certain frequencies of the radiation. The absorbed radiation causes changes in the vibration energy of the chemical bonds. However there must be a net change in dipole moment during vibration in order for the molecule to absorb infrared radiation.

Vibrations of Molecules:

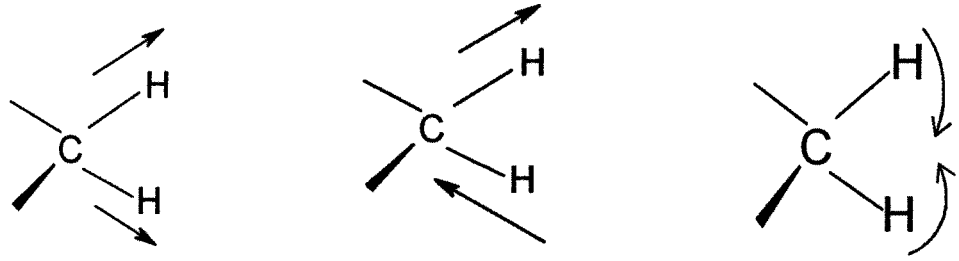
Each molecule has characteristic vibration frequencies. When infrared radiation is incident on a molecule, the vibrating bond absorbs the frequencies matching the natural vibrations of the molecule. The number of fundamental vibrations in a molecule is based on the theory of molecular vibration, which suggests that:

"A molecule composed of n-atoms and has 3n degrees of freedom, 6 of which are translations and rotations of the molecule itself. This leaves 3n-6 degrees of fundamental vibrational (3n-5 if the molecule is linear), 2n-5 cause bond deformation and n-1 cause bond stretching".

Vibration modes are given descriptive names, such as stretching, bending, scissoring, rocking and twisting, but not all modes of vibration absorb infrared light. The simplest types of vibrational motion that give rise to absorptions are:

- ❖ Stretching (asymmetric or symmetric) - the distance between 2 atoms increases or decreases.
- ❖ Bending – the position of the atom changes relative to the original bond axis.

As an example the modes of vibrations of a $-CH_2$ group and its infrared absorption[28] is given below.



Symmetric stretching ($\sim 2850\ cm^{-1}$) | Asymmetric stretching ($\sim 2930\ cm^{-1}$) | Bending vibration ($\sim 1450\ cm^{-1}$)

Figure 10: CH_2 modes of stretching and bending

2.3.1.2 Infrared spectrum

A spectrum is a display of the detector's response which indicates the interaction (i.e. the transmission and absorption of IR light) between the infrared radiation and chemical bonds within the sample. The spectrum presents response as either percentage transmittance (%T) or absorbance (A) on the y-axis and IR frequency in terms of wavenumber (cm^{-1}) on the x-axis. The transmittance is calculated using the equation below.

$$\%T = 100\frac{I}{I_0}$$

Where I is the intensity of the transmitted radiation of a particular frequency and I_o is the intensity of the same frequency of radiation incident on the sample.

Absorbance is inversely and related logarithmically to transmittance through the following equation;

$$A = -\log_{10} T = \log_{10}\left(\frac{I_0}{I}\right)$$

2.3.1.3 Infrared Spectrometer

There are two basic types of IR spectrometer. Early examples of this instrument were of the dispersive types which use prism or grating monochromators to separate the frequencies of the infrared radiation. Dispersive IR spectrometers gave direct measurement of I and I_0 but operation was relatively slow and required sensitive detectors as only a tiny fraction of the source radiation was used at any time. More recently advances in IR technology have led to the development of Fourier Transform Infrared Spectrometers (FTIR). Most modern IR spectrometers use an interferometer. This design of the optical pathway produces an interference pattern known as an interferogram; essentially a plot of intensity against distance. The output from the interferometer is converted to spectrum by the Fourier Transform mathematical procedure. Because of the numerical complexity involved, the adoption of the FTIR was slow. The discovery of a fast Fourier transform (FFT) algorithm by Cooley and Tukey[29] reduced the time for the computer calculation of the spectrum from hours to seconds. With the aid of modern computers FTIR is now used to produce spectra which are significantly superior in terms of signal/noise and acquisition time to those obtained with a dispersive spectrometer.

To obtain the spectrum of a compound, the interferogram of the 'background' which consist of atmospheric gases, CO_2 and H_2O vapour is initially obtained. Fourier transform of the interferogram yields the spectrum of the background. The sample is then placed into the beam and the spectrum is obtained in a similar manner. This spectrum will contain absorption bands for both the sample and the background. The pure spectrum of the sample being analysed is obtained when the software automatically subtracts the spectrum of the background from that of the sample.

The practical improvements of FTIR such as high-speed in acquiring and digitizing the interferogram, increased resolution, optical throughput and lower detection limits makes it particularly favoured compared to the dispersive type of instrument.

2.3.2 Oil Condition Monitoring using FTIR

FTIR is widely used in oil analysis laboratories today. Several studies have shown the effectiveness of this technique for monitoring oil condition[30-34]. It is particularly the ability to detect contaminants and degradation products in used lubricant that is important. The approach provides much information about the oil condition within a relatively short time. The significance of this equipment in oil analysis lies in the fact that it is able to detect low levels of contaminants; it is purely instrument-based and does not require extensive sample preparation or wet chemistry. FTIR therefore presents useful contribution to rapid, simple and economical oil testing.

The infrared spectrum of a used oil sample is typically complex, with mixtures of different molecules such as the additives, base oil components, chemical degradation by-products and contaminants. Nevertheless the unique vibration characteristics of the chemical functional groups within the sample are immediately detected by their infrared absorption, as shown in Figure 11 below.

The increased background absorbance that is frequently observed in used oil samples below 1800 cm^{-1} may be due to the size of suspended carbon particles. Such particles scatter radiation and this wavenumber value corresponds approximately to the reciprocal of the typical particle diameter, where diffraction effects may become significant.

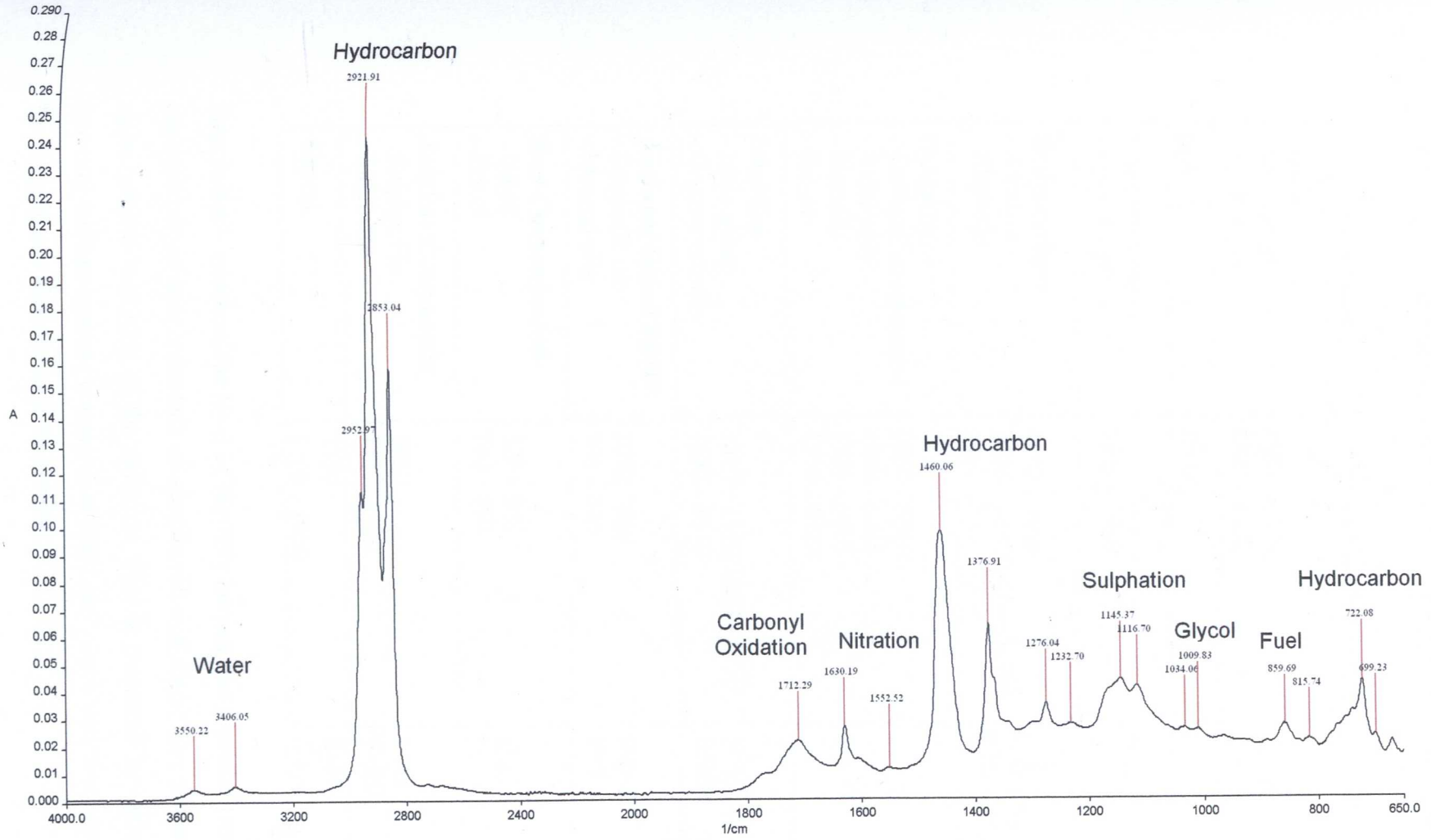


Figure 11: Infrared spectrum of a degraded engine lubricant sample

Table 3: Typical Parameters found in the FTIR Spectra of Used Oils[33-34]

Parameter	Infra-Red Region (cm^{-1})	Vibration
Water - Mineral oil - Synthetic oil	 3500 - 3150 3700 - 3595	O- H
Soot	2000	
Ester Breakdown - Synthetic polyol	 3595 - 3500	O-H
Hydrocarbons - Aromatic - Aliphatic	 3130 - 3000 3000 - 2800/1470 - 1 350 750 - 725	 C-H stretch CH_3, CH_2, CH
Oxidation - Carbonyl compounds, - Aldehydes - Ketones - Esters	 1800 - 1670 1740 - 1725 1725 - 1705 1750 - 1725	 C = O
Nitration - Nitro group - Organic nitrates	 1560 - 1540/1380 - 1350 1650 - 1538	 N=O RNOx
Antiwear loss of ZDDP - Synthetic oils - Mineral oils	 1050 - 960 700 - 640	 P-O-C P=S
Fuel Contamination - Diesel - Petrol	 820 - 800 780 - 750	 C-H
Sulphur Compounds - Sulphoxide - Sulphates	 1050 1180 -1120	 S=O $R-SO_3$
Glycol	3370 1100 - 1020	O-H C-O

Soot Index - measures the level of partially burned fuel particles (soot) in the oil. The characteristic of soot is the lack of specific infrared absorption, rather the soot particles cause general scattering of the radiation. Soot is measured by taking the absorbance intensity with no baseline correction at 2000 cm^{-1}, since very few lubricant components have significant absorbance in this region.

Oxidation Index – measures a variety of combustion by-products such as ketones, aldehydes, and esters. Oxidation products are determined by a general response in the carbonyl region of 1800 - 1670 cm^{-1}. Very few compounds in fresh mineral oils have significant absorbencies in this region; therefore monitoring this region in used oil is a direct measure of oxidation.

Nitration Index - measures nitration products in the region immediately below oxidation. The characteristics of these products absorb in the region of 1650 -1600 cm^{-1}. Monitoring this region directly measures nitration of the used oil.

Sulphate Index - measured in a similar way to oxidation and nitration. Sulphate by-products in used oil have absorbance in the region of 1180 - 1120 cm^{-1}.

Water Index - Water is a strong infrared absorber and is therefore easy to detect. Oil contaminated by water would have significant absorbance between 3700 - 3150 cm^{-1} depending of the nature of the lubricant i.e. mineral or synthetic base component.

Fuel Contamination Index – engine fuel consists of a variety of straight and branched chain aliphatic and aromatic hydrocarbons. Other substituted compounds are included in the formulation. FTIR detects fuel contamination by measuring essentially the absorbance of the aromatic components present in the oil. In contaminated gasoline oil samples absorbance is noticeable at 780 - 750 cm^{-1} and for diesel samples the appropriate wavenimber range is 820 - 800 cm^{-1}.

2.3.2.1 Transmission Technique

Transmission Analysis is one of the most commonly used techniques. The transmission method involves passing infrared radiation completely through a sample and measuring the extent of absorption by the sample. The spectrum however is dependent on sample preparation, concentration, thickness (pathlength), particle size and homogeneity.

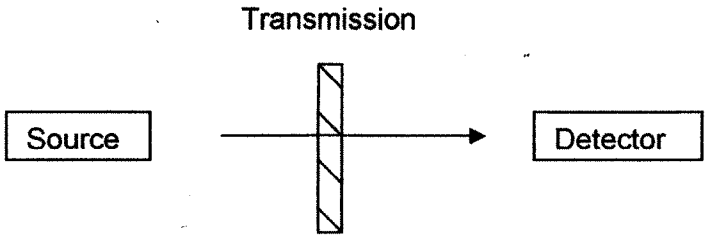


Figure 12: Illustration of the transmission effect

Sample Preparation

The samples analysed were oil samples collected from the Petter engine tests. A drop of oil was placed unto the centre of a potassium bromide (KBR) plate and then a second plate is placed on top of the first plate and clamped together. The pressure from the clamp spreads the liquid which forms a thin film between the two plates. The spectrum was recorded in the range of 4000 - 650 cm^{-1} using 10 scans at resolution 4.0 cm^{-1}. The KBR plates were cleaned with acetone and dried before reused.

Problems in using the transmission technique relates to reproducibility of the pressure exerted on the KBR plates were encountered. It was noticed that the same pressure was not achieved every time and this affected the quality of the resulting spectrum. Collecting a background using the KBR plates also proved difficult. As a result the infrared analysis was carried out using an ATR accessory.

2.3.2.2 Attenuated Total Reflection (ATR) Method

The ATR accessory operates by measuring the changes that occur when the internally reflected infrared beam is exposed to a sample as indicated in Figure 13.

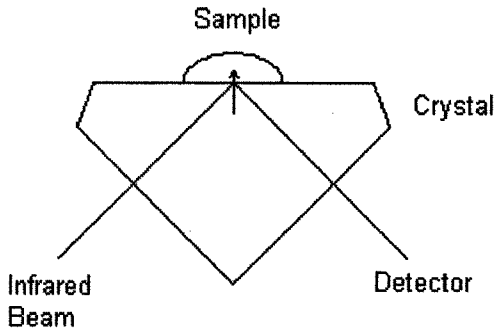


Figure 13: A schematic illustration of the internal reflection effect in a single beam ATR accessory

When an infrared beam at an angle that exceeds the critical angle is introduced onto the crystal internal reflection takes place. This internal reflectance creates an evanescent wave which extends beyond the surface of the crystal into the sample placed on the crystal at a penetrating depth of a few microns (0.5 – 5 μm). The evanescent wave becomes attenuated and passes back to the beam which then egress at the opposite end of the crystal and into the detector of the spectrometer. A spectrum of the samples is then produced.

The quantity of material that is analysed by the evanescent wave however depends on the following criteria:

- the wavelength of the radiation;
- refractive index of the sample;
- refractive index of the ATR crystal;
- optical geometry.

A measure of the quantity of sample is the effective penetration depth of the evanescent wave[35]. This effective depth can be calculated from the following equation;

$$d_p = \frac{\lambda_{air}}{2\pi n_c \left[\sin^2\theta - \left(\frac{n_{r,sample}}{n_{r,c}} \right)^2 \right]^{1/2}}$$

where

$n_{r,c}$ and $n_{r,sample}$ are the refractive indices for the crystal and sample respectively

θ is the angle of incidence at the crystal surface

λ_{air} = wavelength in air. Wavelength inside the crystal is $\lambda_c = \frac{\lambda_{air}}{n_{r,c}}$.

Therefore the absorbance measured by ATR depends on the total path length of sample within the evanescent wave. It is independent of the total volume of sample taken or the thickness of the film used.

ATR crystals are usually materials of high refractive index such as diamond (2.42), Zinc Selenide (ZnSe) (2.49), Thallium Bromoiodide (KRS-5) (2.38), and Germanium (Ge) (4.0).

ATR Experiment Procedure

Samples of new and used lubricant oils collected as described in section 2.2 were analysed using a Perkin Elmer[a] Spectrum One FTIR spectrometer with a Universal diamond ATR accessory installed into the sample compartment. The ATR top-plate is equipped with a small (2 mm) diamond (top) and zinc selenide (ZnSe) bottom crystal. This small area crystal top-plate provides only a single reflection.

The oil sample was delivered onto the diamond crystal with a UL-Tipette. The pipette was suitable for delivering a small quantity of oil as required, preventing overflow of sample. After analysing a sample the crystal was cleaned using hexane moist tissue and subsequently dried with a clean tissue.

Background spectrum and succeeding spectra were acquired using 8 scans over the range of 4000-650 cm^{-1} at a resolution of 4 cm^{-1}. A preliminary test showed that these parameter settings were most appropriate for the oil samples. The resulting spectra were saved in the relevant formats for chemometric analysis.

[a] PerkinElmer® http://las.perkinelmer.com

2.4 Determination of Acid and Base Number of Lubricant Oils

Acid and Base number measurements are among the most frequently used methods for assessing the quality of new lubricants and the condition of used ones. These measures indicate the extent of acid build up and depletion of protective additive in the oil. By definition, finished lubricants are formulated to meet specific applications and are expected to have long service life (6 months to 2 years). However the engine's operating conditions are detrimental to the oxidative and thermal stability of lubricants. Therefore increasing the oil drain interval would certainly increase the degree of oxidation leading to build up of organic and inorganic acids and consequently depletion of additives. These acids, which can corrode engine components, require neutralising to prevent corrosive wear. To facilitate extensions in drain intervals lubricants must have enhanced additives for robust alkaline preservation and acid neutralisation.

A semi-automated system developed by Armitage et al., [1990][36] was used for the acid and base number measurements. Base number analysis was carried out according to the IP 400[37] standard which specifies a conductimetric titration using alcoholic hydrochloric acid as titrant and a solvent mix of toluene, isopropanol and water (500:495:5) by volume. A two platinum plate electrode conductivity cell attached to a conductance bridge was used to measure the conductance of the solution, as acid was systematically added. A major advantage of this technique is the easy determination of the characteristic endpoint. The conductimetric titration is favoured particularly over the previous IP 177 potentiometric titration method[38] as the electrodes do not progressively degrade or require conditioning like the sensitive potentiometric electrodes. This technique was chosen for the BN analysis in this project due to the clear benefits. A modified form of IP 177 using conductimetric endpoint detection was used for acid number measurements.

2.4.1 System Overview

The titration equipment shown in Figure 14 includes the following:

- Platinum electrode conductivity cell connected to an in-house built alternating current (AC) Conductance Bridge;

- HCl acid and KOH base burettes with delivery tubes to deliver metered titrant volumes into the reaction vessel;
- Stirrer connected to 12 volt power supply for mixing solution after addition of titrant;
- Reaction vessel which holds the mixture underneath the conductivity cell, stirrer and delivery tubes;
- Balance used to measure mass of oil sample;
- Computer used to control titrant addition, view titration curve and facilitate storage of data through a GW-Basic programme;
- Printer to obtain tables and figures as required.

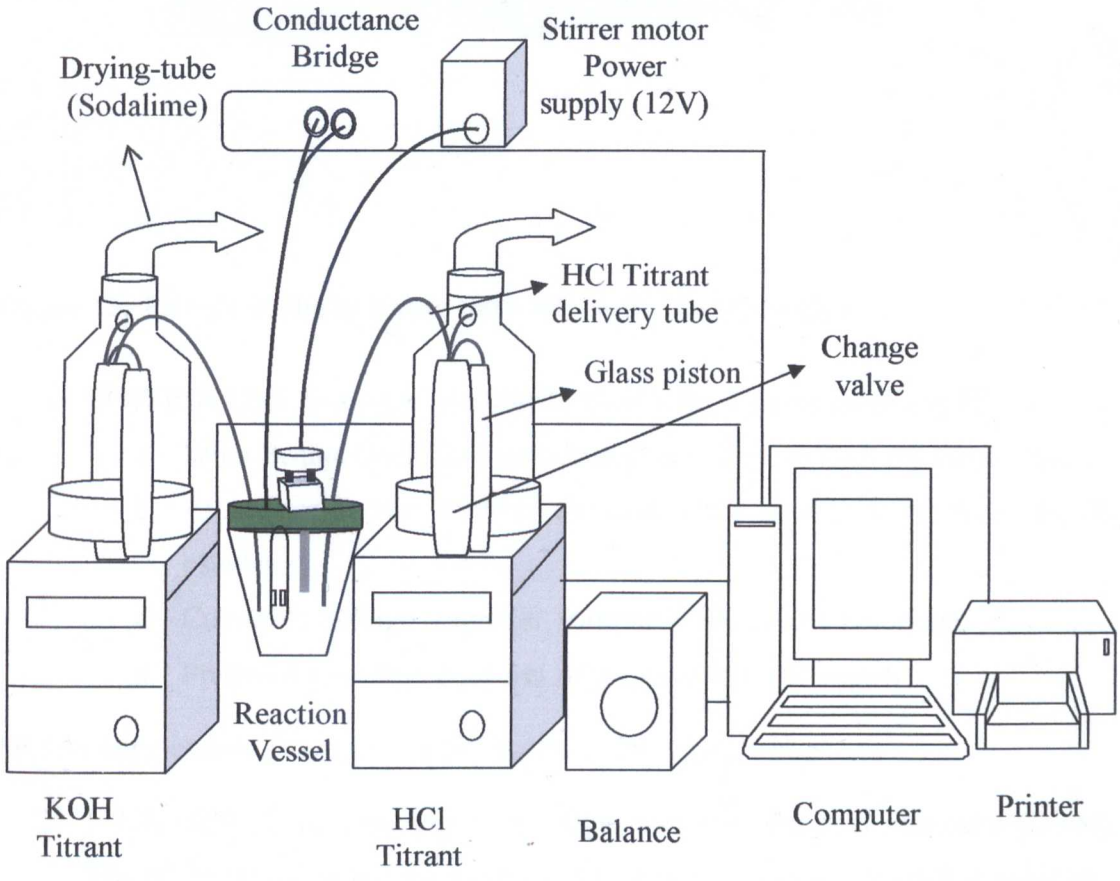


Figure 14: A schematic diagram of the acid/base number titration equipment

The in-house conductance bridge comprises of three main functional parts shown in Figure 15.

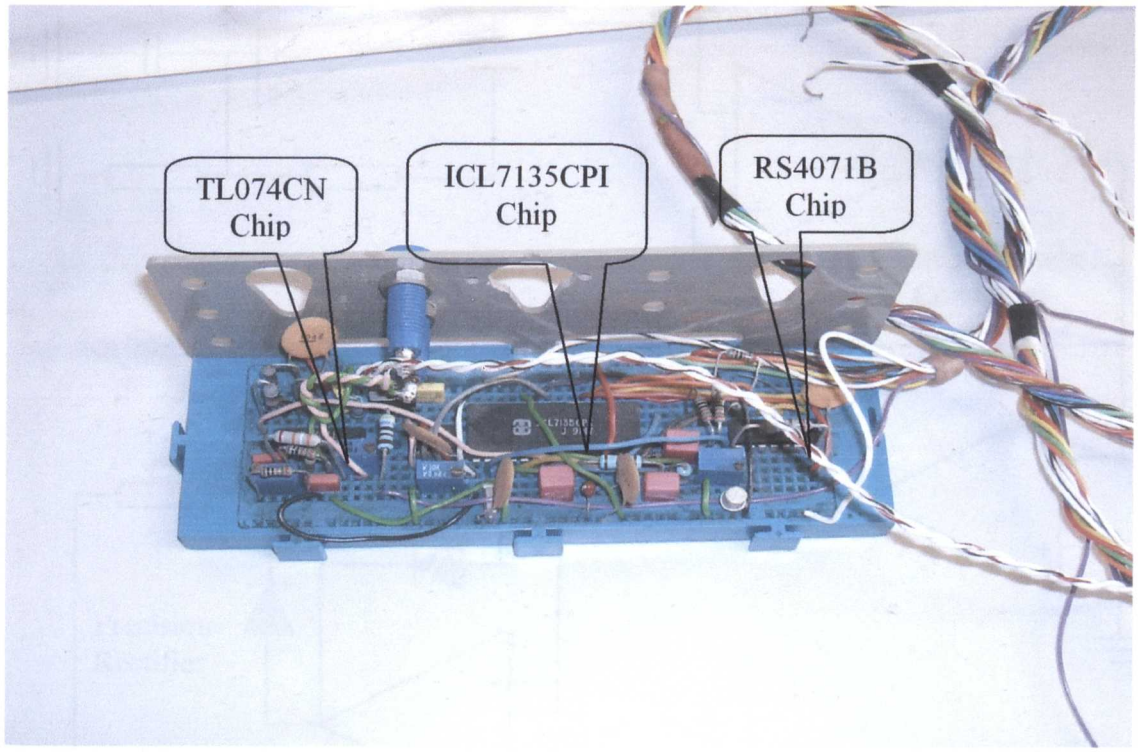


Figure 15: Picture of the in-house built AC conductance bridge

1. TL074CN Chip: analogue integrated circuit with 4 operational amplifiers:
    a. Wien Bridge Oscillator: generates sine waves without any signal input;
    b. Attenuator driver: controls the sine wave amplitude produced by the oscillator;
    c. Current to voltage converter: translates the current to voltage;
    d. Precision Rectifier: converts AC voltage into DC signal.

All four components above correspond to the conductance bridge.

2. ICL7135CPI Chip: analogue to 4.5 digit multiplexed digital voltmeter (DVM). The DVM measures the reactance produced by the conductivity cell in solution.
3. RS 4071B Chip: interface to computer, transfers the DVM readings to the computer were they are displayed in a digital form.

The diagram in Figure 16 illustrates the details of each part.

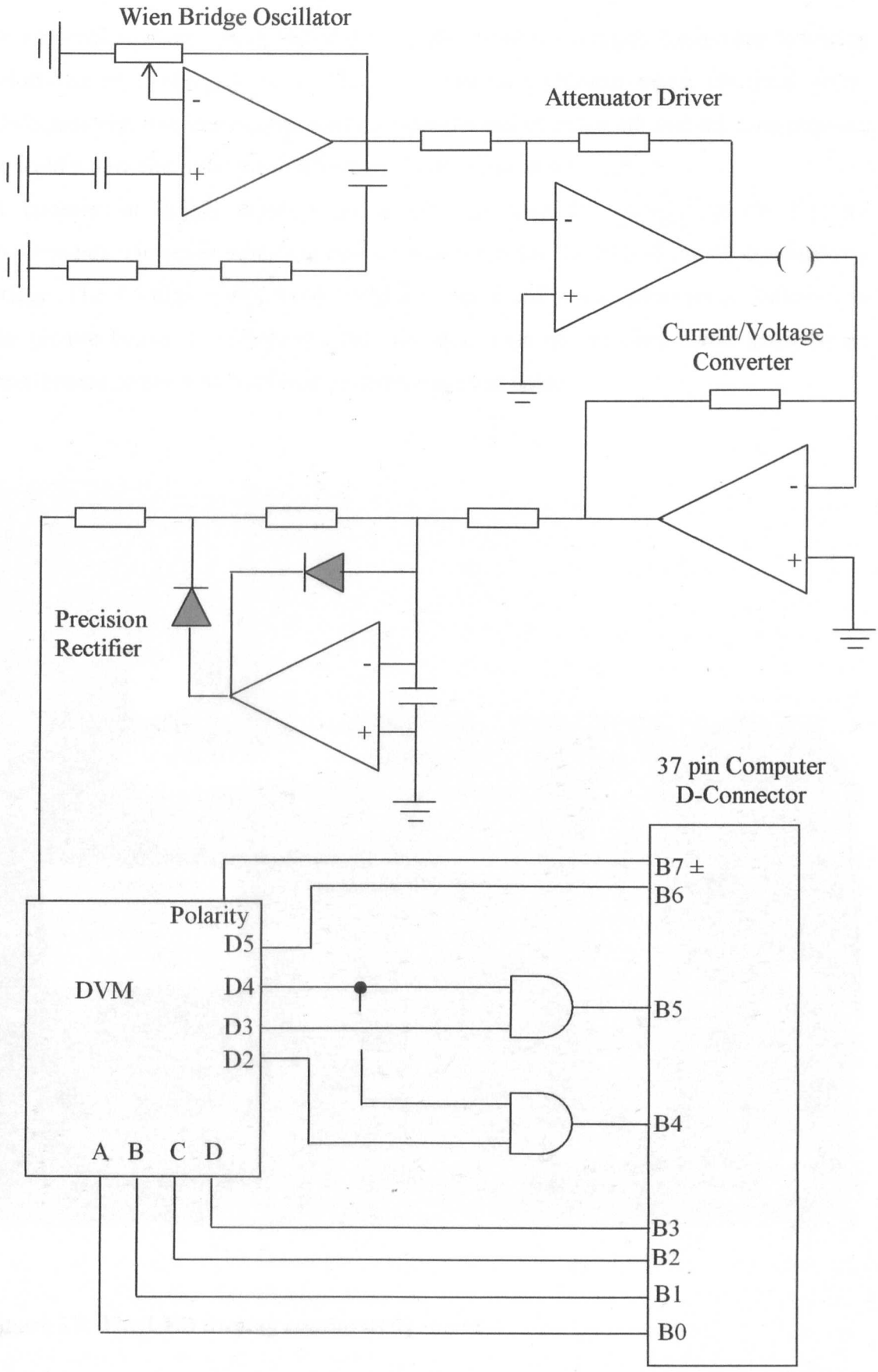


Figure 16: A schematic diagram of the in-house conductance bridge circuit board

Some problems were encountered during the use of the titration equipment following relocation to a new laboratory. The most obvious problem being electrical noise. Unfortunately, this was experienced towards the end of this work and the time required to build a new circuit board was beyond the duration of the research.

A commercial digital conductivity meter was used for completing the titration experiments. However modifications were required for the PTI-18 digital conductivity bridge. The 3.5 digit multiplexed DVM was interfaced to the computer as indicated in the picture below. It is believed that the steel case of the digit meter acted as an interference screen which offered protection against noise.

Figure 17: The LED display conductivity meter

Modification of Stirrer Circuit

The stirrer circuit was also altered, by disconnecting the motor from an independent power supply and reconnecting it directly to the computer's internal 12V supply. The stirrer is activated when the computer is switched on under the control of one I/0 line on the interface card. The schematic diagram below shows the original and modified arrangements of the stirrer circuit.

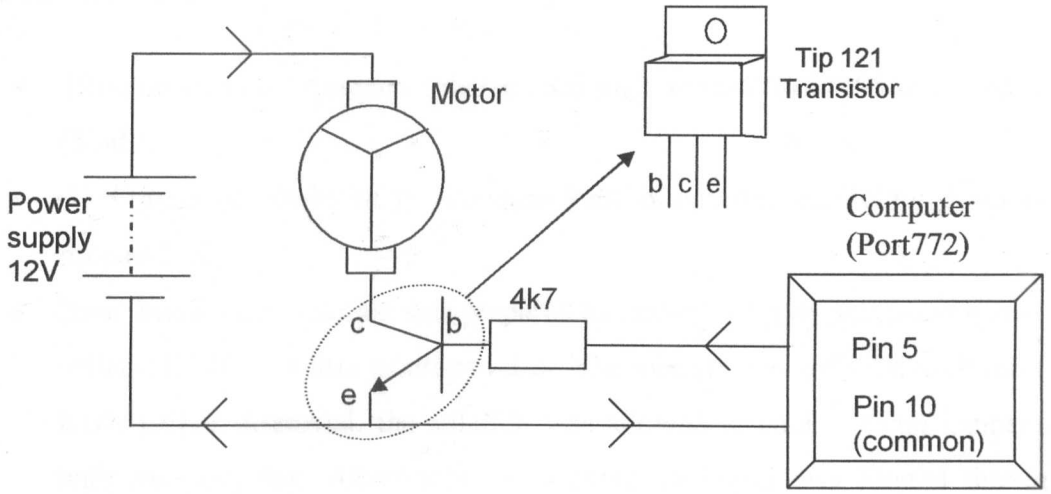


Figure 18: Original stirrer circuit

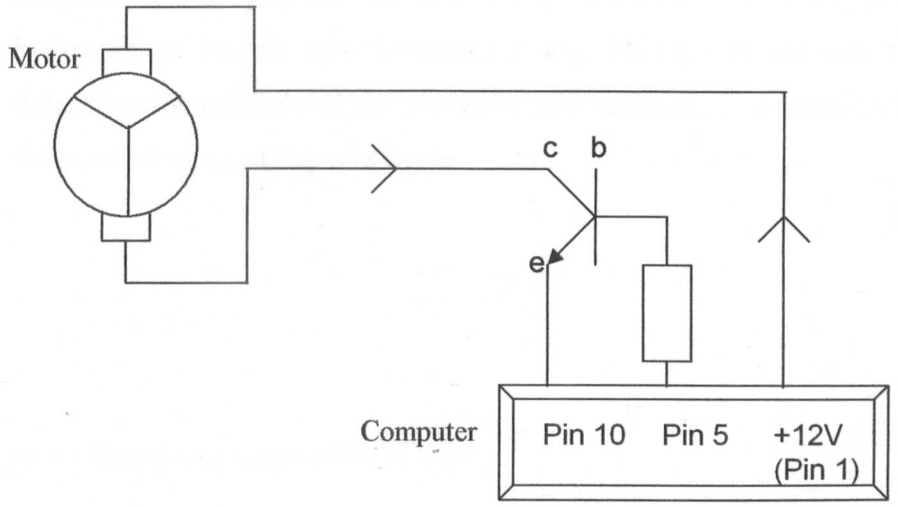


Figure 19: The modified stirrer circuit

It is believed that with this modification the level of interference and noise experienced in the previous system was reduced considerably. This procedure presents a step towards a totally automatic system.

2.4.2 Reagents and Preparation

For the analysis, the following solutions were prepared using analytical grade reagents and distilled water.

- Titration solvent – contains toluene (500 mL), propan-2-ol (495 mL), and water (5 mL).
- Acid titrant (alcoholic HCl) – contains 9 mL of concentrated HCl in 1000 mL of propan-2-ol.
- Base titrant – this solution was prepared by adding 6.3 g of potassium hydroxide pellets (KOH) to 1 litre of propan-2-ol. The mixture was refluxed until the solid KOH pellets dissolved; the solution was allowed to cool at room temperature until the next day. Afterwards the supernatant liquid was filtered through a Buckner filter and stored in a chemically resistant bottle with a drying tube (containing soda lime granules) top in order to protect the KOH solution from atmospheric CO_2.
- Standardization – the acid solution was standardized with a solution of sodium hydroxide of known concentration (0.1M). This procedure was necessary to determine the molarity of the alcoholic acid solution. The equation below gives the concentration of the acid used;

$$c_1 = \frac{c_2 \times V_2}{V_1}$$

Where:

c_1 = unknown concentration of acid;

c_2 = concentration of NaOH used (0.100 mol L^{-1});

V_1 = volume to acid used (8.00 mL);

V_2 = volume of NaOH added (8.30 mL).

$$\text{Acid Concentration} = \frac{0.100 \times 8.30}{8.00} = 0.10375 \text{ mol L}^{-1}$$

This acid solution (0.104 M) was further used to standardise the KOH solution. The concentration of the Base solution was then determined as follows.

$$\text{Base Conc} = \frac{0.104 \times 1.69}{2.0} = 0.0879 \text{ mol L}^{-1}$$

Where: 1.69 mL is volume of acid titrant required to neutralise 2.0 mL KOH solution taken.

All acid and base titrants used during the experiments were prepared to a nominal concentration of 0.1 mol L^{-1}.

2.4.3 Base Number Measurement

Base Number defined by the IP 400/94[37], is the quantity of acid expressed in terms of the equivalent number of milligrams of potassium hydroxide (KOH) per gram of oil sample required to neutralise the alkaline constituent in the sample of oil when titrated under the specified conditions.

The base number measurement was employed in this work as a preliminary method for checking the quality of new oils and to study the resulting degradation arising from service use. Determination of the base number of an oil sample was performed by titrating the oil sample of known mass with acid of known concentration (0.104 M) whilst recording the conductance of the mixture. The specified solvent was used to adjust the total volume of the system. The relationship between the volume of acid added and the conductance of the mixture is shown in Figure 20 for a typical sample.

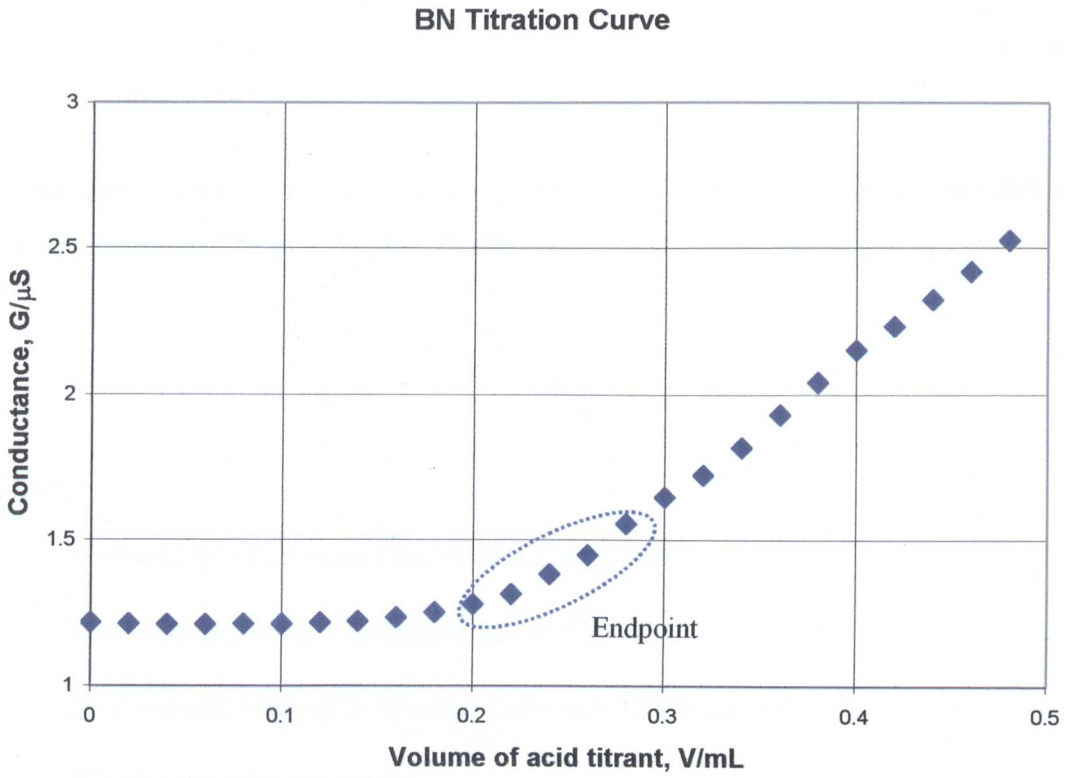


Figure 20: Base number titration curve

The shape of the curve in relation to the titration procedure is described below:

- A measured mass of oil sample was placed in a reaction vessel and solvent was added to dissolve the oil and cover completely the electrodes
- The titration begins with systematic addition of acid to the mixture. The reaction, which occurs slowly, elevates the conductivity of the mixture (creating a line). This corresponds to the acid neutralisation of the base constituents in the oil sample.
- The gradient of the curve rises gently until a region of considerable change in conductivity is reached.
- In the final region the conductance increases rapidly towards the end of the titration (creating a second line). This suggests that in this region the base constituents of the oil are completely neutralised and the solution now contains excess acid. In general acids are good conductors; thus the sustained rise in conductance.

- The point of maximum rate of change in conductance is understood to be the endpoint. This is estimated normally by extrapolation from two intersecting lines.

The endpoint region is indicated on the graph above. The volume of acid, in millilitres, is used to estimate the base number of the sample using the equation below.

$$BN = \frac{V \times M \times 56.1}{W_{Oil}}$$

Where:

V = volume of alcoholic hydrochloric acid (HCl) used;

M = molarity of HCl solution (mol dm^{-3});

56.1 = molar mass of potassium hydroxide (KOH) g mol^{-1};

W_{oil} = mass of oil sample g.

By means of mathematical algorithms new methods for estimating the titration endpoint were integrated into the system. These methods facilitated BN calculation consistently for every sample. The principles behind the mathematical procedures are described in Chapter 3.

2.4.4 Acid Number Measurement

Acid Number - is defined as the quantity of base expressed in terms of the equivalent number of milligrams of KOH per gram of oil required to neutralise the entire acidic constituent in a sample of oil when titrated under the specified conditions.

The conductimetric titration method with the IP 400 solvents system was used to determine the total acid contents of the oil samples. Previous work[39] showed that this technique with the solvent system was a practical means to acid number endpoint estimation. However it was established that the most comprehensible endpoint was achieved via a back titration. The proposed procedure was to initially carry out the

titration using 0.1 mol L^{-1} HCl and then back-titrate with 0.1 mol L^{-1} KOH. A typical resultant graph is shown in Figure 21. The first curve is the reproduced BN curve associated with addition of acid. Following the addition of KOH it was observed that the conductance initially fell then levelled out and finally roses steadily to the end of base delivery.

HCl and KOH are both reasonably strong electrolytes in solution but HCl has significantly higher molar conductivity. The idea of this method was to initially increase the conductance of the solution using the HCl; then decrease the conductance through a second endpoint with KOH. This approach was found to produce a more reproducible titration curve than was ever possible for a direct titration with KOH.

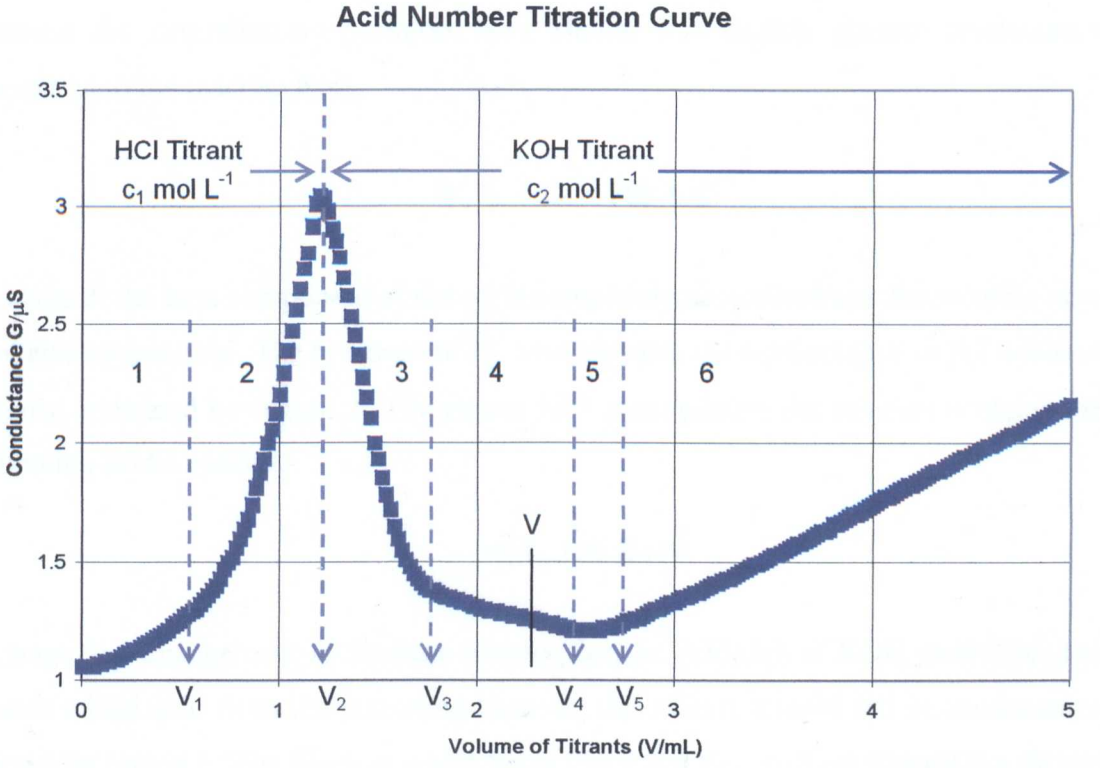


Figure 21: Acid number back-titration graph

The acid number back titration curve is understood to under go six stages as indicated on the graph. Stages 1 and 2 show the region of HCl addition while stages 3 to 6 represent KOH addition. The behaviour of the solution can be described as follows:

In a new oil there are usually no acid components but base additive B^- while in a used oil acid combustion products are present. The acids formed from degradation of the oil constitute the acid content of the oil HA; some of these acids react with the base additive, HX, and some remain unreacted, HY.

$$HA \longrightarrow HX + HY$$

Oil additive reacts with strong acids from combustion/degradation.

$$B^- + HX = HB + X^-$$

In stage 1: addition of HCl titrant neutralises the base present in the oil at the same time chloride salts are formed. The conductivity of the solution labelled 1 increases a little because the neutralisation products have similar but slightly greater conductance compared to the reacting base.

$$B^- + HCl = HB + Cl^-$$

In stage 2: the base component of the oil is completely neutralised and the solution now contains excess acid. The presence of H^+ ions elevates the conductance of the solution rapidly, indicated by region 2. The excess HCl accumulates; the solution contains the following acidic species;

HCL, HB & HY

In stage 3: a change over to the base titration occurs. Addition of KOH neutralises the excess added acid from the preceding titration, this effects a rapid fall in conductance shown by region 3. The reaction which takes place and the products formed are shown below.

$$HCl + OH^- = H_2O + Cl^-$$

In stage 4: neutralisation of the excess added acid is complete. Further reactions occur as the base titrant continues to react with the HB that was formed in the stage 1, and any HB that had originated from reaction with strong combustion acids.

$$HB + OH^- = H_2O + B^-$$

In stage 5: the reaction continues with any acid substances that had accumulated in the oil but were too weak to react with the additive pack alkaline reserve.

$$HY + OH^- = H_2O + Y^-$$

The reaction of these acids is expected to be correlated to a visible change in slope between region 4 and 5.

Finally, in stage 6: reaction is complete and accumulation of excess KOH produces an increase in the conductance of the solution before the end of the titration.

Calculating Acid Number Values

If c_A and c_B represent the concentrations of the HCl and KOH titrants respectively, the amount of HCl used in stage 1 is $c_A V_1$ and the total amount of HCl added is $c_A V_2$. Therefore the excess amount of HCl will be $c_A (V_2 - V_1)$. Where V_1 represents the volume of acid used in stage1, and V_2 the total volume of HCl used.

Neutralising this excess acid requires that

$$c_B (V_3 - V_2) = c_A (V_2 - V_1)$$

$$V_3 = V_2 + \frac{c_A}{c_B}(V_2 - V_1)$$

V_3 represents the total volume of titrants used at the completion of stage 3. This allows a check to be made on the consistency of the titration as V_3 can be calculated from the equation above and measured by either geometric construction or curve fitting the titration curve.

Reversing the first stage also requires that $c_B(V - V_2) = c_A V_2$

$$\therefore V = V_2 + \frac{c_A}{c_B} V_2$$

$$= V_2\left(1 + \frac{c_A}{c_B}\right)$$

For new oil we would expect that V should be identical to V_4 and V_5. With a used oil however V_4 should be greater than V and in some cases V_5 will be even greater still. From these results it is possible to calculate both the strong acid number and the total acid number. Thus

$$\text{Strong acid number} = \left(V_4 - V_2\left(1 + \frac{c_A}{c_B}\right)\right) \times \frac{56.1 c_B}{W_{oil}}$$

$$\text{and Total acid number} = \left(V_5 - V_2\left(1 + \frac{c_A}{c_B}\right)\right) \times \frac{56.1 c_B}{W_{oil}}$$

The difference $\Delta V = V_5 - V$ is a measure of the acid number which is placed in the equation below to estimate the total acid number of the oil sample.

$$AN = \frac{56.1 \times c_B \times \Delta V}{W_{oil}}$$

Where:

56.1 = molar mass of potassium hydroxide (KOH);

c_B = molarity of KOH solution (mol L^{-1});

ΔV = total volume of KOH used to neutralise acids originally present in the oil;

W_{oil} = mass of oil sample (g).

2.4.5 Sample Preparation and Analysis

A programme was written in GW-Basic for the acid and base number analysis (provided in Appendix A). This programme was used to control the titration system. The mathematical algorithm used to determine the titration endpoint which is then used to calculate the base number of a sample was also incorporated into the programme. Approximately 0.7 g (0.690 to 0.790 g) of oil sample was delivered through a tip-pipette into the reaction vessel and 36 mL of solvent was added using a 50 mL zip-pipette. This volume of solvent was enough to cover completely the platinum electrodes. The systematic procedure to carry out acid and base number analysis of new and used oils is illustrated using the diagram in Figure 22.

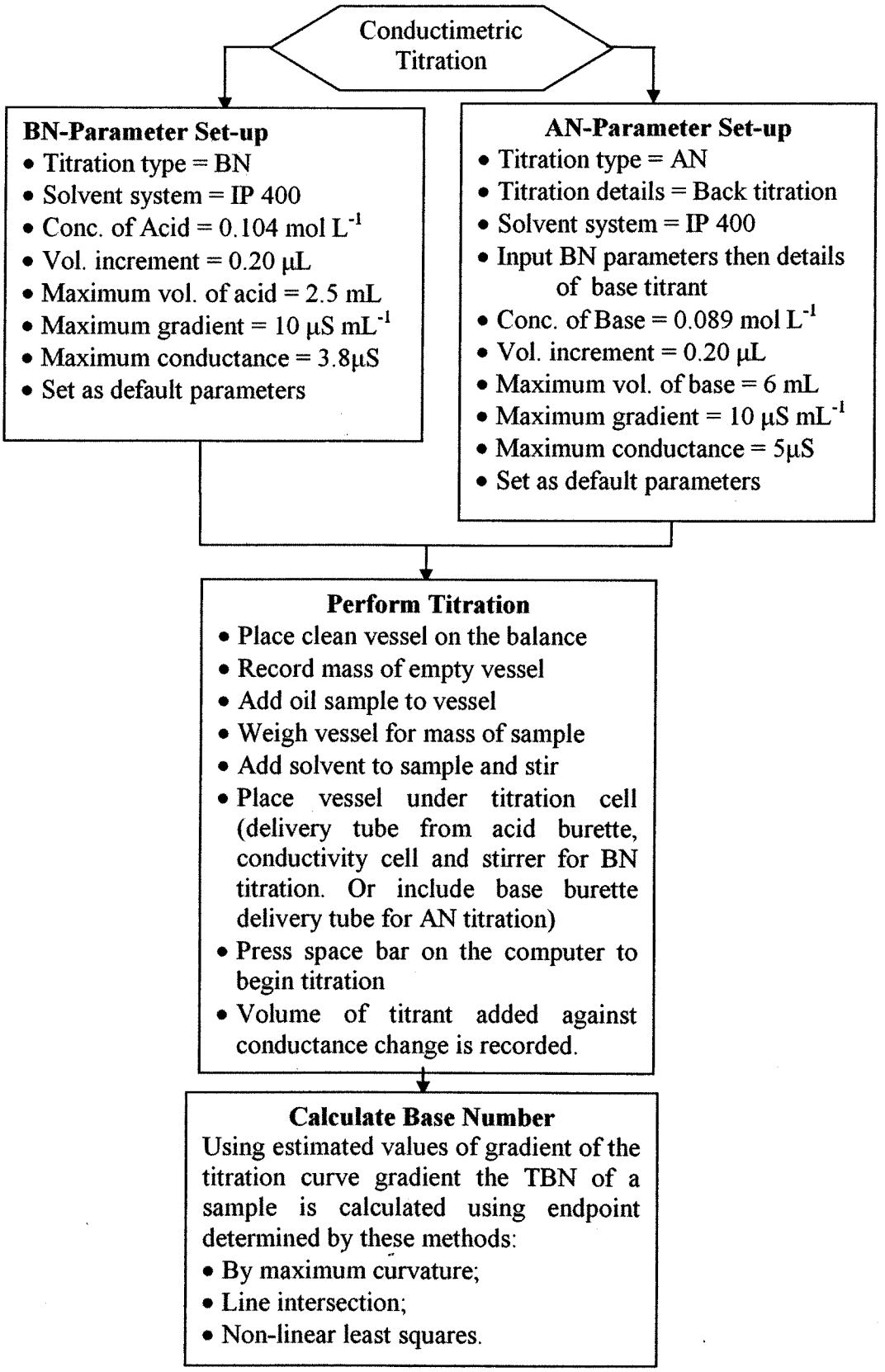


Figure 22: A sequence chart illustrating the GW-Basic programme procedure for the titration

Chapter 3

Chemometric Techniques

Modern analytical instruments and the impact of computers in chemistry is perhaps a key phenomenon of the past generation in chemical analysis. Results from instrumental analyses have led to spectacular growth of data, which requires efficient data processing and management methods. Consequently mathematical/statistical methods that facilitate the interpretation of experimental data are becoming an essential procedure associated with most analytical techniques.

This chapter introduces the mathematical/statistical concepts used in acquiring enhanced information from the diverse data produced from the oil testing experiments described in the Chapter 2.

3.1 An Introduction to Chemometrics

The discipline of chemometrics is often regarded as a key part of new scientific methods although its development dates back over at least the past 30 years if not more. The ideas were proposed for extracting relevant chemical information from experimental data. Data information has become more important today due to growth in data from recent analytical measurements and trends towards higher quality products and greater efficiency in research and industry.

These methods are profoundly dependent on various mathematical principles which demand knowledge of statistics, numerical analysis, and applied mathematics. Several chemometric methods have been used in this work; this chapter aims to explain the concepts that underline the methods employed. These analyses have been carried out using various commercial packages such as SIMPCA-P[40], Minitab[41], Matlab[42], Microsoft Excel[43], and PLS-Toolbox[44].

3.1.1 Definition of Chemometrics

There are many literal definitions for chemometrics but often it is defined by the context of its applications. Several definitions place emphasis on different aspects.

In an early literature review[45] Wold emphases 'that the impact of chemometrics is in the problem solving and not in the data analysis'. Consequently chemometrics must remain

an integral part of all areas of chemistry and adapt statistics to chemistry instead of vice versa.

Given that there are several other definitions within the literature, a reasonable definition [46] which was employed in this research is:

"A chemical discipline that uses mathematical, statistical and formal logic to,

- **design and select optimal experimental procedures;**
- **analyse chemical data to get the maximum relevant chemical information; and**
- **obtain knowledge about chemical data".**

3.1.2 Modelling Methods

A model is an approximate representation of some aspects of reality of a system or process. Models are the chemometric means of extracting information and providing insights into chemical systems. Particularly when complete knowledge of the system is unachievable it is practical to develop a mathematical approximation which best describes the behaviour of the system. Models can be described as follows.

Hard Models: assume that estimated parameters relate to a physical property. So a system is described using the measured parameters as 'independent' variables and the response outputs as the 'dependent' variables. They are commonly derived from well establish theories which are regarded as fundamental laws.

An example is the Beer-Lambert law which gives the linear relationship between the absorbance and concentration of an absorbing species as

$$A = \varepsilon bc$$

Where:

A is absorbance;

ε is the molar absorbtivity;

b is the path length of the sample;

c is the concentration of the sample.

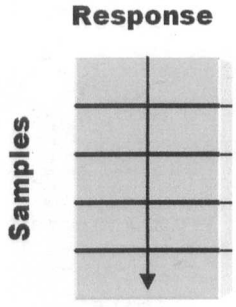
This suggests absorbance is proportional to the concentration of the radiation absorbing species.

Soft Models: addresses a wide range of techniques and tools developed to enhance structured approaches to solve complexities. Instead of defining the problematic parts of a complex system, it aims at creating a similarity which is as close as possible, taking all the complexities into account. This is the usual chemometric approach to data analysis and calibration because soft models can be developed rapidly and tested comparative to hard models. They are also applicable to areas where no true hard model exists. As an example octane number has been accurately predicted from the Raman spectra of gasoline using calibration models[47].

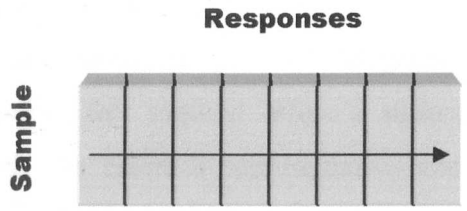
3.1.3 Data Structure

It is believed that the data structure is based on the dimensionality of the data set. Therefore the higher the dimensionality of the data the more powerful the instrument, consequently relevant modelling can be applied. The main categories of data structure are '**Univariate**', '**Multivariate**' and '**Multiway**'.

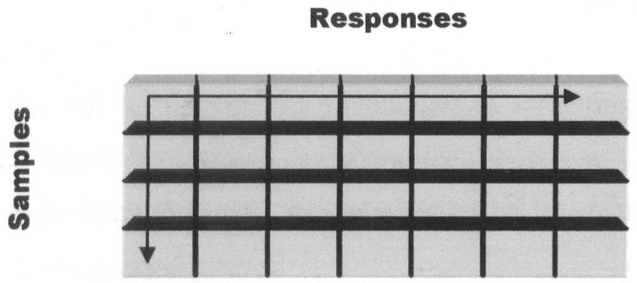
Univariate Data: is the basic type of data with the lowest dimensionality. A typical example involves a PH meter which only gives a single response variable. The data collected forms a column vector that is one-way. It can only vary in one direction indicated by the arrow in the diagram i.e. sample to sample.



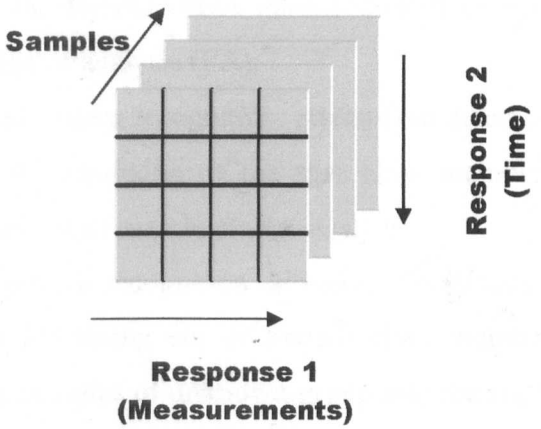
Multivariate Data: analysis of this type of data is common in the literature. Examples of these types of data are spectra or chromatograms which could be a 'one dimensional matrix', that is a sample characterised by several measurements (several columns) or



'two dimensional matrix' which has several samples with multiple measurements varying from sample to sample and measurement to measurements.



Multiway Data: information is organised into a 'three-dimensional array'. An example of this type of data would be measuring the concentration of several samples at several time points. Coupled instrumentation such as GC-MS used to monitor batch processes will give a three way dataset.



3.1.4 Areas of Applications

The main areas of application are generally categorised into four parts.

Experimental Design: this method offers a strategy for experimentation, by using mathematical models to create a representative and informative design that fits the experimental objectives. The method is commonly applicable in three main forms:

a. Screening: identifying important factors and selecting the appropriate ranges for the success of the experiment. Factorial and Placket-Burman are useful methods.
b. Optimization: how to improve and get optimum results by reducing uncontrolled factors which might affect responses. Simplex and central composite designs can be employed.
c. Time saving and robustness: the advantages of screening and optimising allow colossal savings in time which can guarantee robustness.

The methods of experimental design are believed to be invaluable tools for planning, optimising and analysing experiments.

Pattern Recognition: this is one of the first and most publicised areas of chemometrics, particularly useful to chemists since much of chemistry involves using chemical patterns to relate physical information to chemical knowledge. This technique offers three main approaches to describing data.

a. Exploratory data analysis (EDA): provides a visual abstract of the main relationships within a data set. There is no prejudice as to whether or how many groups will be derived. EDA mainly consist of principal component analysis (PCA) and factor analysis (FA).
b. Unsupervised pattern recognition: attempts to detect similarities within a data set without prior knowledge of the true class membership of the samples. The procedure consist of mainly cluster analysis.
c. Supervised pattern recognition: aimed at classification of samples. The method learns from a training set of known class membership, it then attempts to allocate new samples of unknown group into the right classes. There are several methods in this area such as linear discriminant analysis (LDA), partial least squares discriminant analysis (PLSDA) and more recently neural networks used as a nonlinear approach to pattern recognition.

Calibration: many of the achievement in applied chemometrics in the 1980s and 1990s are based on these method with NIR spectroscopy. Calibration is commonly described as an art of using empirical data and prior knowledge for determining how to predict unknown quantitative information Y from measurements X through a mathematical function[48]. As a result calibration is presently used as an alternative measurement technique to reference methods which may be laborious or expensive. This technique divides into:

a. Univariate calibration: this involves relating two single variables x and y together such that x can be used to predict y. For example a single measurement (y) is related to the concentration of a compound (x) by the regression model

$$y = \alpha + \beta x + \varepsilon$$

Where α is the value taken by y when x is zero, β is the rate of increase in y with x (slope) and ε is the random error.

b. Multivariate calibration: this approach utilises more than one predictor variables x to model and predict the target property (y). Several measured x-variables are usually available from the instrument used, for example when a sample is characterized by a spectroscopic method. Some of the methods in this area include Multiple regression, Principal component regression (PCR) and Partial least squares regression (PLSR).

Signal Processing: The technique mainly seeks to extract signal from noise. Most chemical information obtained is in form of signal responses. This approach provides ways of modifying and transforming signals from analytical instruments so results are easily interpreted. This method is usually applied prior to analysis of data that are sequential in time such as spectra or chromatograms. Some of the methods in this area include orthogonal signal correction (OSC), multiple signal correction (MSC), and wavelet analysis.

3.1.5 Effectiveness of Chemometric Models

The methods involved offer many advantages such as:

- swiftness in obtaining real time information from data;
- relevant information can be extracted from less resolved data;
- possibility of improving knowledge about a process;
- improve measurement quality;
- methods are cost effective.

3.2 Principles of the Chemometric Techniques

The objective of this section and the rest of the chapter is to describe the underlying principles behind the methods that were employed for analysis of the experimental data. The projection approach, was mostly used because it offered simpler and visual interpretation of the data. The outline of the techniques employed is as follows:

- Descriptive method;
- Pre-processing method;
- Exploratory/Pattern recognition method;
- PLS and PLS discriminant method;
- Curve Fitting method.

3.3 Descriptive Method

The major characteristics of a dataset are described, based on the type of variables involved (single or multiple). Descriptive statistics provide a simple summary of the sample data. The methods involved can be used to describe the basic features of the data. The outcomes are presented in either numerical or graphic mode as appropriate. The numerical approach, such as the mean and standard deviation are more precise and objective, whereas graphs are better for visual assessments.

3.3.1 Univariate Analysis

This technique was used for analysing single parameter measurements. Analyses of this type were carried out using the following methods.

Sample Mean: most commonly used measure of the central tendency for a dataset. Technically known as the "measure of location" the mean of a data set x is the sum of

all the variables divided by the total number of variables n. The arithmetic mean, which was mostly used, is given as:

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n}$$

Standard Deviation: is the most common measure of dispersion. It is used to measure how widely spread the values in a dataset are around their mean. The standard deviation of a sample is estimated by:

$$s = \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n-1}}$$

If the data are close to the mean, then the standard deviation is low or close to zero. Conversely a high standard deviation indicates the data deviate widely from the mean.

3.3.2 Multivariate Analysis

The procedures involved are used to measure and interpret the relationship between multiple variables.

Analysis of Variance (ANOVA): is a statistical procedure which tests for significance differences among the means of two or more groups on one or more variables. ANOVA models may be used for identifying the source of variation within measured parameters. There are several types of ANOVA depending on their application to experimental data. A one-way ANOVA test was employed for comparing the means of the three proposed methods for estimating base number titration endpoint. A good summary of the one-way ANOVA formulae [49] is presented below:

Source of Variation	Degrees of Freedom (DF)	Sums of Squares (SS)
Between groups	$h-1$	$\frac{\sum_i T_i^2}{n} - \frac{T^2}{N}$
Within groups	by subtraction	by subtraction
Total	$N-1$	$\sum_i \sum_j x_{ij}^2 - \frac{T^2}{N}$

where $N = nh$ = total number of measurement

n is the number of samples per group

h is the number of groups

T_i is the sum of the measurement in the ith sample

T is the sum of all the measurement

The test statistic $F = \frac{\text{between - sample mean square}}{\text{within - sample mean square}}$ and the critical value is $F_{h-1, N-h}$.

Covariance: is a measure of how two variables vary together. The covariance of two variables x_j and x_k is defined by

$$Cov(x_j, x_k) = \frac{\sum_{i=1}^{n} (x_{ij} - \bar{x}_1)(x_{ik} - \bar{x}_k)}{n-1}$$

The covariance becomes more positive for each pair of values which differ from their mean in the same direction, and becomes more negative with each pair of values which differ from their mean in opposite directions.

The equation above is equivalent to the equation below which is commonly used in matrix calculations. If X is a column of vectors with a scalar random variable (n), given that μ_k is the expected value of the k^{th} element of X then the covariance matrix Σ is define as:

$$\Sigma = [(X - E[X])(X - E[X])^T]$$

This covariance matrix is a very useful tool in many different areas, for example a transformation matrix can be derived that allows one to completely uncorrelate the data matrix and use to find an optimal basis for representing the data in a compact way such as Principal Components Analysis (PCA).

Correlations: the correlation coefficient provides a measure of the strength of a linear association between two variables. If the relationship between two variables gives a positive slope then the coefficient is positive, conversely the coefficient is negative if the association has a negative slope. However if the variables are linearly independent their correlation will be zero.

The most commonly used coefficient is the *Pearson product-moment correlation coefficient* also known as the "sample correlation coefficient" is obtained by dividing the covariance of the two variables by the product of their standard deviations. The Pearson correlation coefficient is written:

$$r_{12} = \frac{\sum_{i=1}^{n}(x_{1i} - \bar{x}_1)(x_{2i} - \bar{x}_2)}{(n-1)s_1 s_2}$$

A correlation coefficient of +1 indicates an increasing linear relationship with ideal correlation between variables; while −1 indicates a decreasing linear relationship and exact inverse correlation whereas values in between indicates the degree of linear dependence between the variables.

Geometrically the correlation coefficient of an uncentered dataset can be viewed as the cosine of the angle between the two vectors of samples drawn from the two variables.

The methods described in this section have been used when necessary to provide summary statistics for the experimental data.

3.3.3 Multivariate Projection Methods

The principles of projection are based on the point that the fundamentals of multivariate data analysis (MVDA) can be summarised in terms of the geometry of multidimensional spaces[50]. For this reason, multivariate data and models can be represented as points, lines, planes and hyperplanes in such spaces (K-space). The

ability to understand structures in two and three dimensions can be generalised to higher dimensional spaces extended by the use of many variables.

Assume a data table with M=3 column variables (x_1, x_2, x_3), each variable will define a coordinate axis in 3-D coordinate space. Each row variable (observation) of the data table is characterise by the numerical values of X and are represented by one point in the M-space as indicated in Figure 23. Therefore a swarm of points can define all the observations of X.

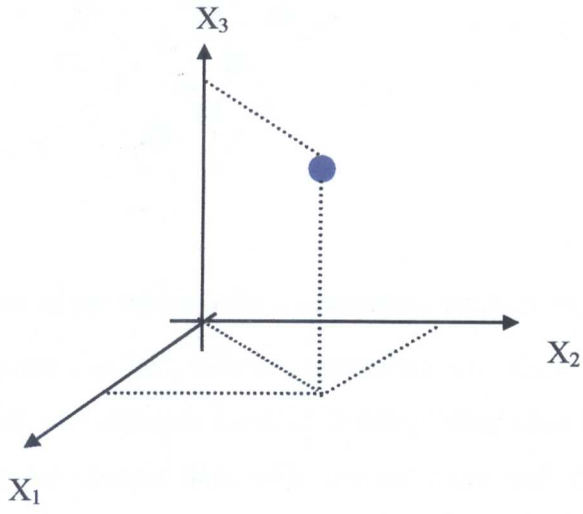


Figure 23: Illustrating a row variable (observation) as a point in K = 3 space

The idea of describing the observations of a data table as points in space makes it possible to convert the table into a graph.

The ability to represent three variables in a three-dimensional space can also be extended to a larger number of variables (K) in K-space. The K-space representation is constructed by allowing each of the K X-variables to define one orthogonal axis in coordinate space. However such a space is impossible to visualise. Therefore 2-D and occasionally 3-D space are used for modelling these complex spaces.

By use of mathematical models a meaningful description of the outline of the swarm points can be achieved. The model can be viewed as a window in a defined space (M=3) which is oriented such that it provides an overview of the data. The principle behind this procedure is known as **projection**.

Figure 24 below illustrates how the data points are projected onto a 2-D plane from its original three 3-dimesional space.

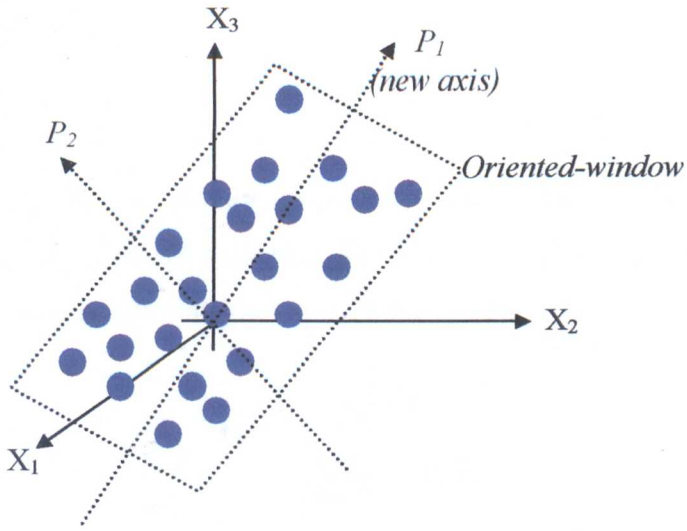


Figure 24: Projection of variables onto a plane that enables overview of the data

The projection technique can be extended mathematically from 2-D and 3-D to higher number of dimensions. For example a model of lower dimension window can be placed in the M-space of a set spectra data with several rows and 3351 column variables (M=3351), the data points are projected onto this plane which can be extracted and displayed as a simpler 2-D or 3-D plot.

The projection principle is a prime composition of most of the chemometric methods employed in the analysis of the experimental data.

3.4 Pre-processing and Enhancement of Data

A multivariate data set may contain variables that have measurements on different scales. The methods of pre-processing are used to reform the data and the results effectively simplify data interpretation. So the model interpretations are true assumptions of all the variables and not the dominant variables. All chemometric methods are influenced by the data pre-processing method as a result they are performed prior to modelling.

Pre-processing may often be referred to as '**Scaling**' and can be applied in several ways depending on the modelling objectives and prior knowledge about the data properties. The techniques used are discussed below.

Mean Centring: this procedure is carried out by subtracting the mean of each column from each variable in the data set so the sum of each column is now zero.

$$^{ctr}x_{ij} = x_{ij} - \bar{x}_j$$

Standardising: this procedure usually occurs after mean centring; the mean centred variable is divided by its standard deviation. The scaled variables now have equal unit variance. This type of scaling is also known as "Unit variance" or "auto-scaling".

$$^{std}x_{ij} = \frac{x_{ij} - \bar{x}_j}{\sqrt{\frac{\sum_{i=1}^{I}(x_{ij} - \bar{x}_j)^2}{I}}}$$

This procedure puts all the variables on approximately the same scale. Hence variables of low numeric values assume equal significance to those of high values.

Pareto scaling: this type of scaling gives each variable a variance equal to its initial standard deviation rather than unit variance. The scaling weight is

$$\frac{1}{\sqrt{^{std}x_{ij}}}$$

Selective scaling: is useful for dataset of several measurement types. It is possible to divide the variables into blocks and perform separate scaling on each block.

3.5 Exploratory Method

Exploratory data analysis (EDA) is a procedure that utilizes several (mostly graphical) techniques for data analysis. The methods are usually used to enhance insights to data by:

- uncovering underlying structure by extracting important variables and detecting outliers and anomalies;
- testing underlying assumptions and developing practical models that can establish optimal factors.

Unlike statistical models EDA postpones the usual assumptions about the data and uses the direct approach of allowing the data itself to reveal its underlying structure. Most EDA techniques are graphical in nature with a few quantitative techniques since the main aim is to explore the data.

3.5.1 Principal Component Analysis (PCA)

PCA is one of the most widespread chemometric techniques, and in many ways forms the basis for multivariate data analysis[51-52]. The first use of PCA can be linked to the famous earliest publication in statistics by Karl Pearson in 1901[53]. He described the analysis as finding "*lines and planes of closest fit to systems of points in space*". However the fundamental ideas are based on eigenanalysis; a method well known for much longer to physicists and mathematicians. Since the 1930s and 1940s the utility of PCA has been rediscovered in many diverse scientific fields.

In chemistry, PCA was initially introduced around 1960 but it wasn't until the 1970s that the first major chemical applications were reported[54-55]. PCA is the foundation of many chemometric methods.

Definition for PCA

PCA is described as a mathematical procedure, which finds orthogonal transformations of a set of correlated variables into a new set of uncorrelated variables (principal components) by rotating the data onto new axes in the space defined by the original variables. This rotation is projected in such a way that the new axes lie along the direction of maximum variability with constraints that the axes are orthogonal.

These new uncorrelated variables are linear combinations of the original variables and are formed sequentially in such a way that the first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible subject to the orthogonality criteria.

3.5.1.1 Mathematical Derivation of Principal Components

Let $X^T = [x_1, x_2, \ldots\ldots x_p]$ be a p-dimensional variable with mean μ and covariance matrix Σ. The aim is to find new sets of variables $Z = (z_1, z_2, \ldots\ldots z_p)$ that are

uncorrelated and the variance decreases in order of significance. The approximation of each z_j is obtained by a linear combination of the original variable X;

$$z_j = a_{1j}x_1 + a_{2j}x_2, \ldots\ldots, a_{pj}x_p$$

$$= a_j^T X = \left(a_{1j}, a_{2j}, \ldots\ldots, a_{pj}\right)\begin{pmatrix} x_1 \\ x_2 \\ \vdots \\ x_p \end{pmatrix}$$

where $a_j^T = \left(a_{1j}, a_{2j}, \ldots\ldots, a_{pj}\right)$ is a vector of constants.

So that the overall transformation is orthogonal, a normalisation constraint that the sum of the squared coefficients be equal to unity $a_j^T a_j = \sum_{k=1}^{p} a_{kj}^2 = 1$ is imposed.

The first principal component (PC1) is derived by means of the linear transformations given as

$$z_1 = a_1^T X$$

where the coefficient vector a_1 is chosen such that the variance of z_1 is maximised subject to the normalisation constraint;

$$Var(z_1) = Var\left(a_1^T X\right)$$
$$= a_1^T \Sigma a_1$$

Then vector a_1 is determined by maximising $Var(z_1)$ subject to $a_1^T a_1 = 1$.

The maximisation is expressed as multivariate differential equations using Lagrange multipliers (a method that finds the extrema of a multivariate function subject to one or more constraints) and setting the derivative of the expectation to zero.

So let λ be the Lagrange multiplier that maximises $Var(z_1)$.

By differentiation of

$$L(a_1) = a_1^T \Sigma a_1 - \lambda\left(a_1^T a_1 - 1\right)$$

$$\frac{\partial L}{\partial a_1} = 2\Sigma a_1 - 2\lambda a_1$$

and setting the derivative equal to zero

$$\frac{\partial L}{\partial a_1} = 0$$

indicates that

$$(\Sigma - \lambda \mathrm{I})a_1 = 0.$$

A non-zero solution for a_1 is obtained only when $(\Sigma - \lambda \mathrm{I})$ is a singular matrix. Hence a_1 is determined to be the eigenvector of the covariance matrix Σ which corresponds to the eigenvalue $\lambda \equiv \lambda_1$.

As a result PC 1 is determined when the variance is maximised

$$Var(z_1) = a_1^T \Sigma a_1$$
$$= a_1^T \lambda_1 \mathrm{I} a_1 = \lambda_1$$

so λ_1 is the largest eigenvalue of the covariance matrix, and PC 1 retains the maximum amount of sample variation.

The second principal component (PC 2) is obtained in a similar way. However in addition to the normalisation constraint a second constraint is imposed.

To derive PC 2 ($z_2 = a_2^T X$), the next coefficient vector a_2 maximises $Var(z_2)$ subject to two constraints; that $a_2^T a_2 = 1$ and $Cov(z_2, z_1) = 0$ (i.e. PC 2 should be uncorrelated to PC 1). Given that

$$Cov(z_2, z_1) = Cov(a_2^T X, a_1^T X)$$
$$= a_2^T \Sigma a_1$$

and since $\Sigma a_1 = \lambda_1 a_1$ an equivalent condition is that $a_2^T a_1 = 0$. This indicates that a_1 and a_2 should be orthogonal.

In order to maximise the variance of z_2 two Lagrange multipliers denoted λ and δ are used as;

$$L(a_2) = a_2^T \Sigma a_2 - \lambda(a_2^T a_2 - 1) - \delta a_2^T a_1.$$

Differentiation with respect to a_2 gives

$$\frac{\partial L}{\partial a_2} = 2(\Sigma - \lambda \mathrm{I})a_2 - \delta a_1 .$$

For the variance of z_2 to be a maximum $\frac{\partial L}{\partial a_2} = 0 \quad \therefore\ 2(\Sigma - \lambda \mathrm{I})a_2 - \delta a_1 = 0 .$

Multiply this equation on the left by a_1^T to obtain

$$2a_1^T \Sigma a_2 - 2\lambda a_1^T a_2 - \delta a_1^T a_1 = 0$$

Since

$$a_1^T a_2 = 0,\ a_1^T \Sigma a_2 = 0 \text{ and } a_1^T a_1 = 1$$

it follows that

$$\delta = 0$$

when

$$\frac{\partial L}{\partial a_2} = 0 .$$

The derivative condition then becomes

$$(\Sigma - \lambda \mathrm{I})a_2 = 0 .$$

So a_2 is also an eigevector of the covariance matrix Σ whose eigenvalue $\lambda \equiv \lambda_2$ is the second largest. PC 2 retains the next maximum of the remaining sample variation.

In general[56]

$$Var(z_k) = a_k^T \Sigma a_k = \lambda_k$$

where:

- k^{th} largest eigenvalue of the variance of the k^{th} PC;
- the k^{th} PC (z_k) retains the k^{th} greatest fraction of the variation in the sample.

PCA has the characteristic of being the most favourable linear transformation for keeping the subspace of largest variance.

The main use of this method is to reduce the dimensionality of a data set while retaining most of the information. A data set with significant correlation will have many fewer PCs than the number of original variables. Consequently, the effective dimensionality of the data can be reduced to a smaller number (usually two or three) without losing much

of the information. The PC may also reveal variables that determine some inherent structure in the data which may be interpreted in chemical or physico-chemical terms.

Due to the complexity of these mathematical procedures the calculations are hardly ever done by hand, instead algorithms are implemented into computer programs. There are several algorithms used in performing PCA the most common are Singular Value Decomposition (SVD) [57-58] and Non-linear Iterative PArtial Least Squares (NIPALS) [59-60].

A PCA algorithm is used to provide an approximation of a data matrix X, (with N rows and K columns) in terms of the product of two matrices T and P, which capture the essential patterns in the data.

$$X = T \cdot P + E$$

where:

- X is the original data matrix;
- T a matrix that contains as many rows as the original data matrix, and known as the "Scores";
- P a matrix that contains as many columns as the original data matrix, and known as the "Loadings";
- E is the residual matrix.

Each scores matrix consists of a series of column vector t_a and each loadings matrix a series of row vectors p_a, one for each of the principal components. The first scores vector and loadings vector are called the eigenvectors of the first principal components, thus each successive component is characterised by a pair of eigenvectors.

A projection of the data matrix unto the plane of the principal components is illustrated by the complementary set of score and loading plots. When the columns t_a in the score matrix are plotted against each other (t_1 vs. t_2) a scatter plot of the observations is revealed. An equivalent loadings plot (p_1 vs. p_2) show the variables projected unto the plane of principal components.

3.5.1.2 NIPALS Algorithm for PCA

This is an iterative algorithm which extracts components one at a time. This method is useful in the case of large datasets.

Step 1: Initiation

If required the data matrix is first pre-processed (e.g. standardised or mean centred) to give a matrix X.

Step 2: New Principal Component

From the original matrix X the column with the largest sums of squares (i.e. largest variance) is used as the first guess of the sores first principal component ${}^{initial}\hat{t}$.

Step 3: iteration for the principal component

Calculate a guess loading vector

$${}^{unnorm}\hat{p} = \frac{{}^{initial}\hat{t}' \bullet X}{\sum \hat{t}^2}.$$

The guess of the loadings is normalised as

$$\hat{p} = \frac{{}^{unnorm}\hat{p}}{\sqrt{\sum {}^{unnorm}\hat{p}^2}}$$

and then calculate a new guess of the scores

$${}^{new}\hat{t} = X \bullet \hat{p}'$$

Step 4: A check for convergence (indicates if the PC has been extracted)

$$\sum \left({}^{initial}\hat{t} - {}^{new}\hat{t} \right)^2$$

If this value is exceeds a threshold ${}^{new}\hat{t}$ replace ${}^{initial}\hat{t}$ and the calculation is repeated from step 3.

Step 5: Computation of component and calculation of residuals

$${}^{resid}X = X - t \bullet p$$

Step 6: Further PC's

The next PC is computed by substituting the residual data matrix for X and then back to step 2.

3.6 Partial Least Squares Regression and Discriminant Methods

3.6.1 Partial Least Squares Regression (PLS)

PLS was first introduced by Herman Wold in the late sixties in the field of Econometrics. Around 1980 the chemometric adaptation of PLS was developed by the groups of Svante Wold and Harald Martens[61] for chemical applications. The simplest PLS-model was shown to be robust compared to traditional methods of regression. To give a more descriptive meaning, PLS is interpreted by means of *Projections to Latent Structures.*

PLS is used to find the relationship between two matrices (X and Y), that is a latent variable approach to modelling the covariance structures in these two spaces. A PLS model will try to find the multidimensional direction in the X space that explains the maximum multidimensional variance direction in the Y space. Thus the model aims to extract factors from X matrix that are relevant to Y response.

Similarly to PCA, the matrix X is reduced to sets of PLS factors which are formed by transposing the correlated variables into new uncorrelated variables which are linear combinations of the original variables. The PLS factors are formed sequentially so the first factor accounts for most of the covariance of X with the response Y, and the second accounts for the next largest remaining variation whilst being orthogonal to the first and so on until the last PLS factor accounts for all the covariance with Y.

3.6.1.1 Mathematics of PLS

PLS regression specifically seeks for a set of components (called latent variables) that performs a simultaneous decomposition of X and Y with the constraint that these components explain as much as possible of the covariance between X and Y. These factors are orthogonal linear combinations of the original variables. The latent variables are chosen such that maximum correlation with the dependent variable is formed. A PLS model thus contains the smallest necessary number of factors[62].

PLS based on singular value decomposition of X^TY gives:

$$X^TY = \Sigma a_i \, f_i \, g_i^T$$

where f_i and g_i are orthonormal vectors of suitable dimensions, a_i are the singular values arranged in decreasing order. The largest singular value a_1 is given by

$$a_1^2 = \max\left(f^T X^T Y g\right)^2 \quad \text{with } |f| \text{ and } |g| = 1$$

here $|f|$ is the length of the f vector.

The way PLS works is described by the following inequality:

$$s_i^2(A - B) \geq s_{i+k}^2(A) = a_{i+k}^2$$

where $s_i(A)$ is the i^{th} singular value of matrix A and B is a matrix of rank k. When the inequality is applied we get

$$s_1^2\left(X_{i+1}^T Y\right) = s^2\left(X_i^T Y - p_i t_i^T Y\right) \geq s_2^2\left(X_i^T Y\right)$$

which shows that the largest singular value at step $i+1$ is larger than the second largest singular value as step i. Therefore only one component is selected at a time in the PLS technique. However the singular value is taken as

$$\left(s_1\left(X_i^T Y\right)\right)^2 = \max f^T X_i^T Y Y^T X_i f \quad \text{for } |f| = 1$$

so if

$$
\begin{aligned}
\left(s_1\left(X_{i+1}^T Y\right)\right)^2 &= \max f^T X_{i+1}^T Y Y^T X_{i+1} f \\
&= \max f^T \left(I - p_i w_i^T\right) X_i^T Y Y^T X_i \left(I - w_i p_i^T\right) f \\
&\leq \max f^T X_i^T Y Y^T X_i f \\
&= \left(s_1\left(X_i^T Y\right)\right)^2 \quad \text{for } |f| = 1
\end{aligned}
$$

It follows that what is taken from $X_i^T Y_i = X_i^T Y$ constantly decreases, therefore one can select components until $s_1(X_i Y)$ is minimal.

A PLS algorithm models the relationship between the two blocks of variables X and Y. There is a regression step where the decomposition of X is used to predict Y. The PLS model is considered as having outer relationships for X and Y individually and an inner connection of the two blocks. The outer relations of X and Y blocks are:

$$X = TP^T + E = \sum t_h p_h^T + E$$

$$Y = UQ^T + F = \sum u_h q_h^T + F$$

Where q is a normalised vector, this is similar to a loadings vector.

The T and P for PLS differ to those obtained in PCA. Unique sets of scores and loadings are obtained for each compound in the dataset. For example if there are 15 compounds of interest, there will be 15 sets of T, P and Q.

3.6.1.2 NIPALS Algorithm for PLS

The basic PLS built on the NIPALS algorithm developed by Wold et.al[63] is presented below.

Initiation

If required the data matrices X and Y are scaled. Then

First PLS component

1. Set u to the first column of Y.

2. Calculate w using

$$w = \frac{X^T u}{u^T u}.$$

3. Calculate the guess scores using the normalised w with

$$t = \frac{X w}{w^T w}.$$

4. Calculate c using

$$c = \frac{Y^T t}{t^T t}.$$

5. Calculate a new vector u using normalised c from

$$u = \frac{Y c}{c^T c}.$$

6. Check for convergence; if the $\sum \left({}^{initial}\hat{t} - {}^{new}\hat{t} \right)^2$ value is minimal proceed to 7 if not the calculation is repeated from 2.

7. X-loadings: $p = \frac{t^T X}{t^T t}$

8. Y-loadings: $q = \frac{u^T Y}{u^T u}$

9. find regression coefficient $b = \frac{u^T t}{t^T t}$

10. calculate residual matrices ${}^{resid}X = X - tp^T$ and ${}^{resid}Y = Y - btc^T$

Subsequent PLS components are calculated by replacing X and Y by the residuals and repeat from 1.

Only a single stage is required when there is only one y-variable known as PLS 1. If there are several y-variables then more stages are required; this situation is known as PLS k.

3.6.2 Partial Least Squares Discriminant Analysis (PLS-DA)

This model is based on the PLS technique which consists of an X-matrix of explanatory variables and Y matrix of response variables. The PLS-DA model rotates the projection to give latent variables that maximise class separation and also provides information about X-variables that contribute to the separation. However the Y-block in a PLS-DA model is a categorical one which defines class membership by assuming a numerical value of 1 if an observation is a member of a class and 0 if otherwise.

X-Matrix	Y-Matrix		
	A	B	C
A (10)	1	0	0
B (12)	0	1	0
C (9)	0	0	1

Figure 25: Illustration of a dummy Y-matrix used to setup class membership for each category in the X-matrix

A PLS-DA model does not allow other response variables other than the one defining the class membership; consequently, all the X-variables share the same task with respect to the class assignment.

3.7 Curve Fitting Methods

This section describes the methods used in fitting the base number titration curve. These techniques were employed for estimating the titration endpoint.

3.7.1 Linear Least-Squares Estimation

The method of least squares is an optimisation technique which is commonly used for estimating parameters or fitting an equation to data points. The technique finds a function which best approximates the data by minimizing the sum of squares of the deviations between the actual data and model predicted data.

Least-squares quadratic: is the line with the minimum sum of square deviations that fits through the specified data points. Assume the model function is a quadratic equation of the form $Y = \beta_0 + \beta_1 X + \beta_2 X^2$. At each point ($X_i$, Y_i) we can write

$$Y_i = \beta_0 + \beta_1 X_i + \beta_2 X_i^2 + \varepsilon_i$$

for $i = 1, 2....n$. β_0 specifies the intercept and β_1 the initial slope; and β_2 half the initial curvature; ε_i represents residual at point (X_i, Y_i).

The least-squares procedure finds parameter values, β_0 and β_1, β_2, that minimize the *residual sum of squares*; ε^2, where $\varepsilon^2 = \sum_{i=1}^{n} \varepsilon_i^2$. It follows that

$$\varepsilon^2 = \sum_{i=1}^{n} \left(Y_i - \hat{Y}_i\right)^2 = \sum_{i}^{n} \left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right)^2$$

where ε^2 is the quantity to be minimised.

Differentiating the equation above with respect to each of the parameters and setting the results to equal zero gives:

$$\frac{\partial \varepsilon^2}{\partial \beta_0} = -2\sum_{i=1}^{n} \left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) \therefore \sum_{i=1}^{n} \left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) = 0;$$

$$\frac{\partial \varepsilon^2}{\partial \beta_1} = -2\sum_{i=1}^{n} X_i \left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) \therefore \sum_{i=1}^{n} X_i \left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) = 0;$$

$$\frac{\partial \varepsilon^2}{\partial \beta_2} = -2\sum_{i=1}^{n} X_i^2\left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) \therefore \sum_{i=1}^{n} X_i^2\left(Y_i - \beta_0 - \beta_1 X_i - \beta_2 X_i^2\right) = 0.$$

These conditions form 3 simultaneous linear equations:

$$\beta_0 n + \beta_1 \sum_{i=1}^{n} X_i + \beta_2 \sum_{i=1}^{n} X_i^2 = \sum_{i}^{n} Y_i ;$$

$$\beta_0 \sum_{i}^{n} X_i + \beta_1 \sum_{i=1}^{n} X_i^2 + \beta_2 \sum_{i}^{n} X_i^3 = \sum_{i}^{n} X_i Y_i ;$$

$$\beta_0 \sum_{i}^{n} X_i^2 + \beta_1 \sum_{i=1}^{n} X_i^3 + \beta_2 \sum_{i}^{n} X_i^4 = \sum_{i}^{n} X_i^2 Y_i .$$

The least-squares fitting quadratic was integrated into the GW-basic programme that operates the titration procedure. The algorithm implemented carried out calculations in matrix form as shown below.

Given that $y = a_1 + a_2 x + a_3 x^2$ and that the x variables which involve an odd number, $2n+1$, are centred on zero the x values are -n, -n + 1,...., -1, 0, 1, ..., n -1,n. The system is described by an overdetermined set of $2n+1$ equations for the 3 unknown's a_1, a_2, and a_3, of the form

$$\begin{bmatrix} 1 & -n & n^2 \\ 1 & -n+1 & (n-1)^2 \\ \vdots & \vdots & \vdots \\ 1 & 0 & 0 \\ \vdots & \vdots & \vdots \\ 1 & n-1 & (n-1)^2 \\ 1 & n & n^2 \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \\ a_3 \end{bmatrix} = \begin{bmatrix} y_{-n} \\ y_{-n+1} \\ \vdots \\ y_0 \\ \vdots \\ y_{n-1} \\ y_n \end{bmatrix}$$

which can be written as

$$(\mathrm{X})\underline{a} = \underline{\mathrm{y}}$$

The least-squares solution is obtained by pre-multiplying by the matrix transpose X^{T}

$$\mathrm{X}^{\mathrm{T}}\mathrm{X}\,\underline{\mathrm{a}} = \mathrm{X}^{\mathrm{T}}\underline{\mathrm{y}}$$

to obtain a 3×3 coefficient matrix and then inversion to give

$$\underline{a} = \left((\mathrm{X})^{\mathrm{T}}(\mathrm{X})\right)^{-1}(\mathrm{X})^{\mathrm{T}}\,\underline{\mathrm{y}}.$$

This can be viewed as

$$\underline{a} = (\mathrm{Y})\underline{y}$$

in which the matrix (Y) is dependent only on the value of n.

3.7.1.1 Estimating Gradient and Curvature

From the expressions used to fit a quadratic curve to the data, values for the gradient and curvature, particularly at the central value $x = 0$ are obtained. These values are used to find initial estimates for the non-linear least-squares model. This approach was also employed as a method for estimating the titration endpoint from the curvature. Given that

$$y = a_1 + a_2 x + a_3 x^2$$

First differentiation with respect to x gives

$$\frac{dy}{dx} = a_2 + 2a_3 x$$

The gradient, when $x = 0$ is thus simply a_2

Taking the second derivative with respect to x gives

$$\frac{d^2y}{dx^2} = 2a_3 .$$

Hence when $x = 0$ $\dfrac{d^2y}{dx^2} = 2a_3$.

These values for curvature are used to find the volume at which the titration curve has maximum curvature. This method has proved to be much more reliable than simple difference methods for estimating second derivatives.

3.7.1.2 Intersecting Least-squares Lines

The two least-squares lines fitted to the titration curve is indicated in Figure 26 below. The least-squares line were fitted as follows:

1. a first least-squares line is drawn through the data points from the initial stage of the titration, where conductance is almost constant;
2. the second least-squares line is fitted through the data points from the later stage of the titration where conductance is increasing rapidly due to excess acid.

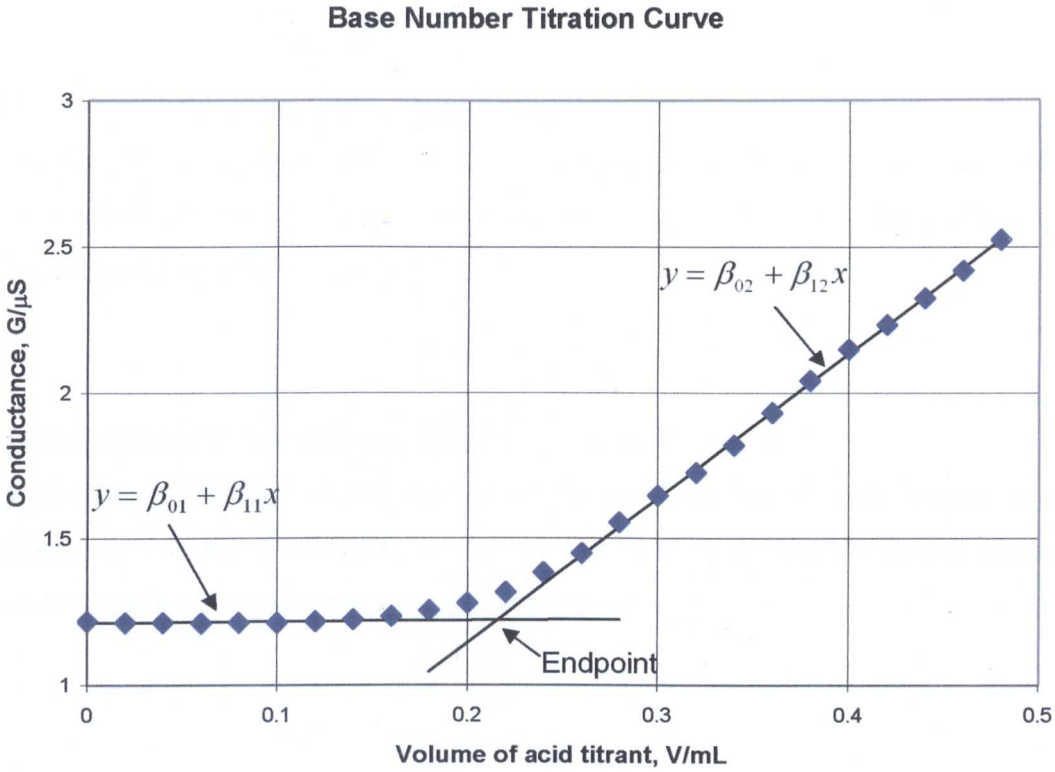


Figure 26: Illustrating the intersection of two least-squares line fitted to the base number titration curve

The intersection of these lines gives an estimate of the endpoint volume, V. At the intersection

$$\beta_{01} + \beta_{11}\mathrm{V} = \beta_{02} + \beta_{12}\mathrm{V} \quad \therefore \mathrm{V} = \frac{\beta_{01} - \beta_{02}}{\beta_{12} - \beta_{11}}.$$

The volume of acid at this point is believed to be the quantity required to completely neutralise all the alkaline components of the oil sample. The estimated endpoint volume was then used to calculate the base number of the sample using the equation below

$$BN = \frac{V \times M \times 56.1}{W_{oil}}$$

where M is the concentration of the acid and W_{oil} is the mass of oil used in the titration. A detailed description of the errors associated with such a calculation can be found in reference 64.

3.7.2 Nonlinear Least-Squares Estimation

The nonlinear model developed for fitting the titration curve data is described below. The estimation involved fitting the nonlinear model by least-squares. An example of a nonlinear model may be written as:

$$Y = a_1 + \frac{a_2}{X + a_3}$$

the output variable Y is a nonlinear function of the input variable X.

In nonlinear models one of the derivatives of the response Y with respect to the parameters (a_1, a_2, a_3) is a function of at least one of those parameters. In this example differentiating Y with respect to the parameters gives:

$$\frac{\partial Y}{\partial a_1} = 1,$$

$$\frac{\partial Y}{\partial a_2} = \frac{1}{(X + a_3)}$$

and

$$\frac{\partial Y}{\partial a_3} = \frac{-a_2}{(X + a_3)^2}.$$

since the resulting derivatives involve at least one of the parameters the model is recognised as nonlinear.

Similar to linear models the parameters are calculated so the least-squares condition $\sum_{i=1}^{n} \varepsilon_i^{\,2} = \sum_{i=1}^{n} \left(Y_1 - \hat{Y}_i\right)^2$ (the sum of squares of the residuals) is minimised. The minimum sum of squares is obtained by a numerical method which uses iterative calculations. The

iterative method begins with initial estimates of the p parameters, $a_1, a_2, ..., a_p$. These are successively improved until the sums of squares of the residuals converge to a minimum.

The model employed in this work is shown below.

$$\varepsilon^2 = \sum_{i-1}^{n} \left(Y_i - \hat{Y}_i\right)^2$$

$$\frac{\partial \varepsilon^2}{\partial a_k} = -2\sum_{i=1}^{n} \left(Y_i - \hat{Y}_i\right)\left(\frac{\partial \hat{Y}_i}{\partial a_k}\right) \quad k = 1, 2, 3, ..., p$$

For ε^2 to be a minimum these derivatives must be simultaneously zero. That is

$$\sum_{i=1}^{n} \left(Y_i - \hat{Y}_i\right)\left(\frac{\partial \hat{Y}_i}{\partial a_k}\right) = 0 \quad k = 1, 2, 3, ..., p$$

Let us assume that improved values for the parameters can be obtained in the form

$$a_k := a_k + \delta a_k \quad \text{k} = 1,2,3,....\text{p}$$

leading to a new calculated values

$$\hat{Y}_i := \hat{Y}_i + \sum_{j=1}^{p} \left(\frac{\partial \hat{Y}_i}{\partial a_j}\right) \delta a_j$$

where the derivatives are calculated using the current estimates of the a_k value. The simultaneous equations now become

$$\sum_{i=1}^{n} \left(\varepsilon_i - \sum_{j=1}^{p} \left(\frac{\partial \hat{Y}_i}{\partial a_j}\right) \delta a_h \right) \left(\frac{\partial \hat{Y}_i}{\partial a_k}\right) = 0 \quad k = 1, 2, ..., p$$

On rearrangement the expression

$$\sum_{j=1}^{p} \sum_{i=1}^{n} \left(\frac{\partial \hat{Y}_i}{\partial a_j}\right)\left(\frac{\partial \hat{Y}_i}{\partial a_k}\right) \delta a_j = \sum_{i=1}^{n} \varepsilon \left(\frac{\partial \hat{Y}_i}{\partial a_k}\right) \quad k = 1,2,...., p$$

is obtained.

This set of p equations is solved for the p unknowns $\delta a_1, \delta a_2, ..., \delta a_p$.

These are used to create new estimates of the parameters

$$a_k := a_k + \delta a_k \quad k = 1,2,\ldots,p$$

The derivatives $\left(\frac{\partial \hat{Y}_i}{\partial a_k}\right)$ are recalculated and the simultaneous equations are again solved until all of $\delta a_1, \delta a_2, \ldots, \delta a_p$ are judged to be negligible.

The existence of a solution and the speed of conversion depend to a considerable degree on the accuracy of the initial estimates of the parameters and the nature of the non-linear function.

3.7.2.1 Derivation of the Nonlinear Least-squares Model

The basic shape of the BN titration curve is given in Figure 27 below; this includes the shapes of the first and second derivatives with respect to the input variable V (volume of acid titrant).

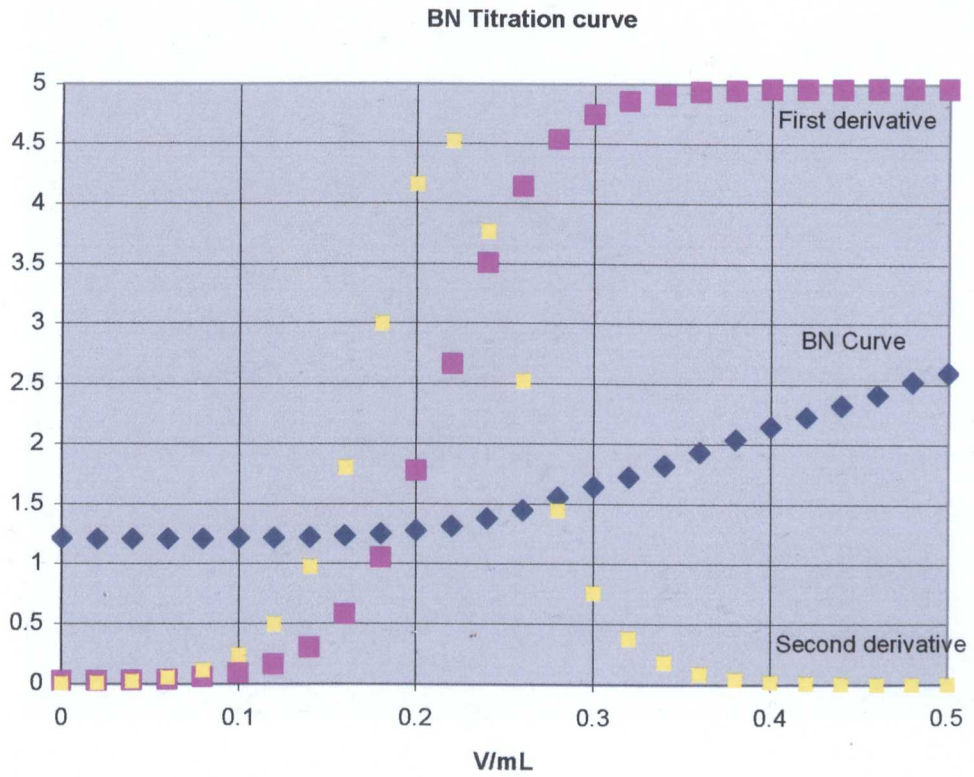


Figure 27: BN titration curve with the first and second derivatives.

Since the titration curve data is the relationship between the conductance of the mixture and volume of acid added, the curve is essentially two straight lines joined by a curve section. The first derivative is a step or wave shaped curve and the second derivative has the shape of a peak. For this reason a model defined by differential equations was considered appropriate for fitting the curve because of the apparent simplicity of the second derivative.

The three possible curves with the shape of a simple peak considered are:

1. Exponential function $\frac{d^2y}{dx^2} = e^{-x^2}$

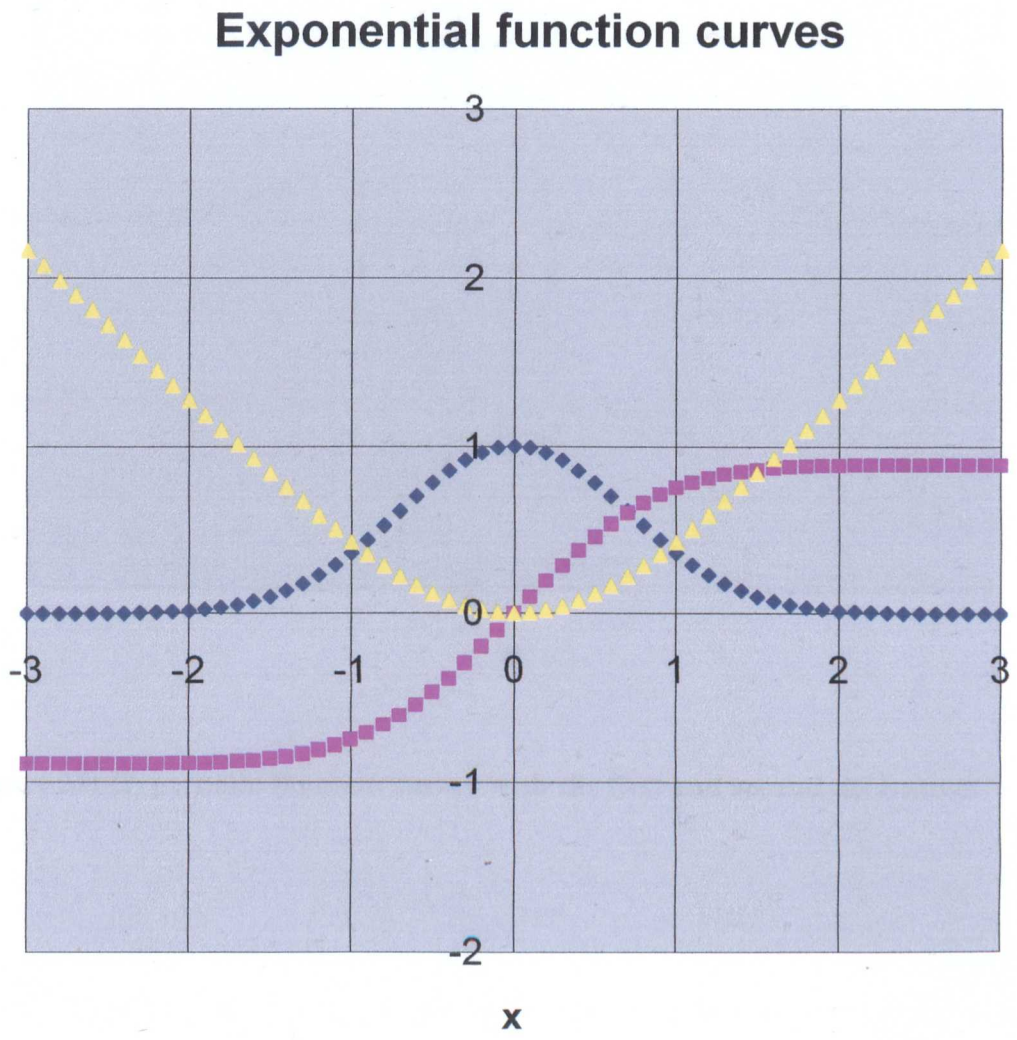


Figure 28: Exponential curves with the first and second derivatives

2. Hyperbolic function $\frac{d^2y}{dx^2} = \text{sech}^2(x)$

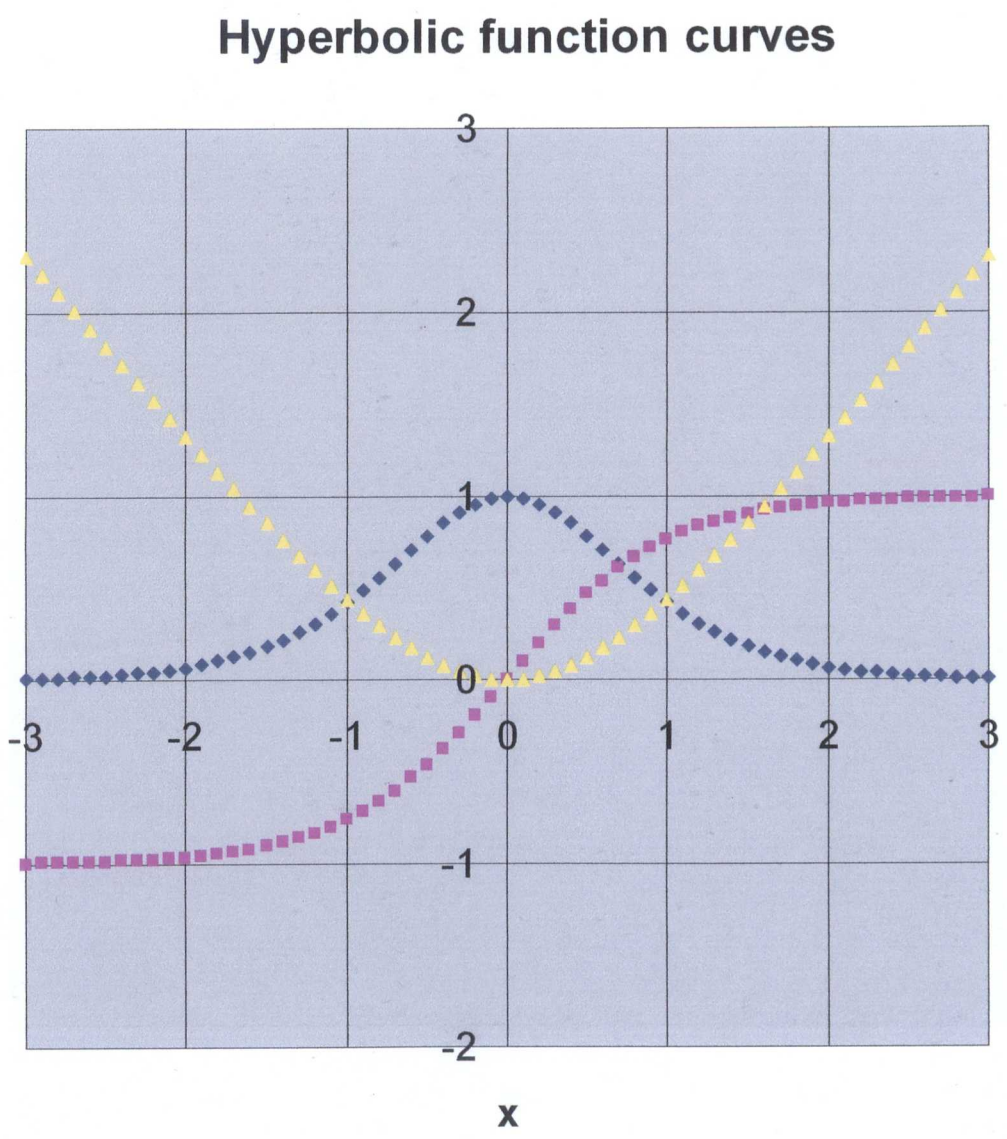


Figure 29: Hyperbolic function curves with the first and second derivatives

3. Rational function $\frac{d^2y}{dx^2} = \frac{1}{1+x^2}$

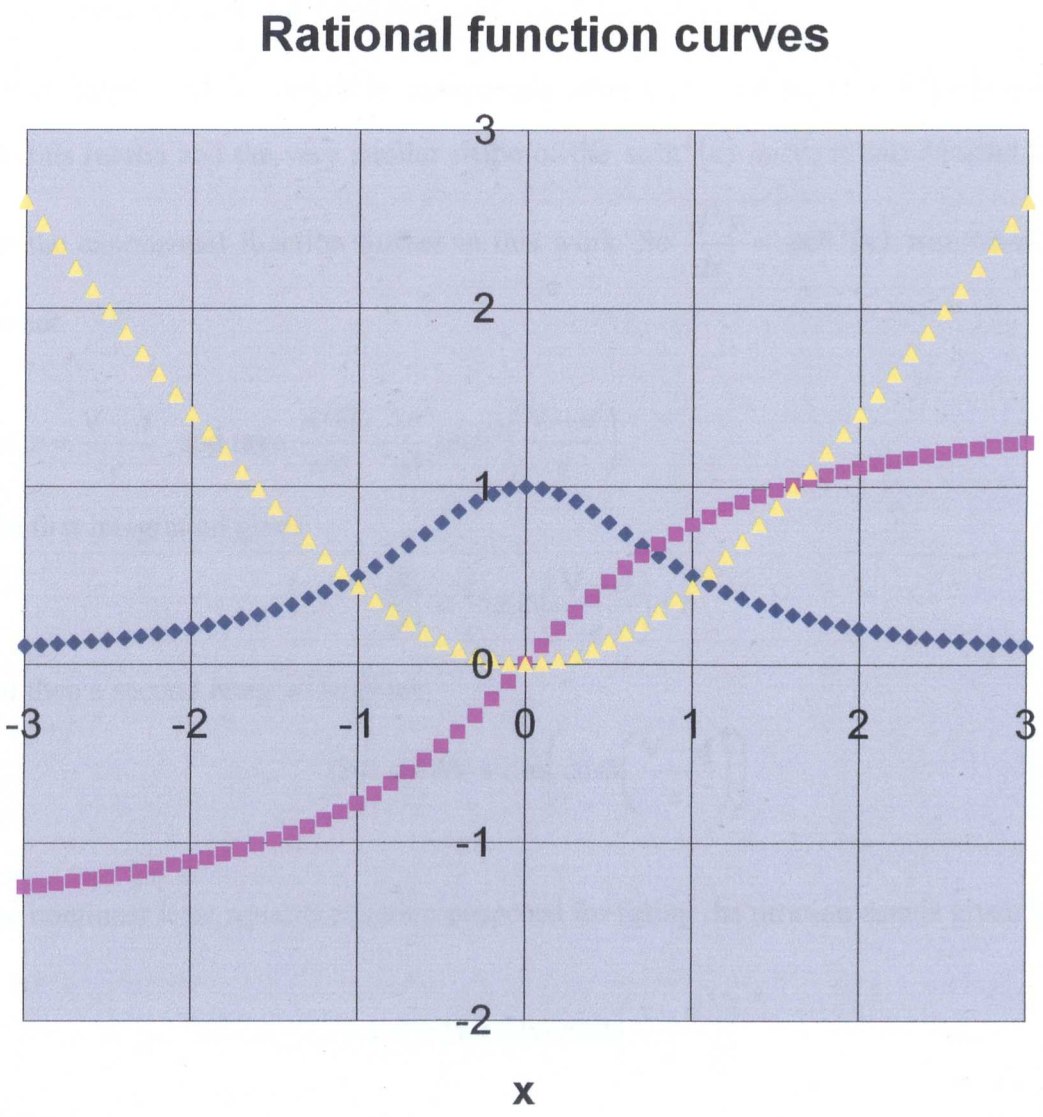


Figure 30: Rational function curves with the first and second derivatives

Each curve has a maximum value for $\frac{d^2y}{dx^2}$ of 1 when $x = 0$. The curves along with their first and second integrals with respect to x are shown in Figure 28, 29 and 30. For each of the function, the integrals were shown with integration constants such that $\frac{dy}{dx} = 0$ and $y = 0$ when $x = 0$.

To apply such a function however these curves must conform to the following criteria:

- the final function and its first derivative must be easily evaluated in a computer program;
- the shape, size and position of the peak can be adjusted.

The curve of $y = e^{-x^2}$ cannot be analytically integrated twice for G as a function of V. For this reason and the very similar shape of the $\text{sech}^2(x)$ curve it was decided not to use the exponential function further in this work. So $\frac{d^2y}{dx^2} = \text{sech}^2(x)$ was considered further.

Let $x = \frac{\text{V} - d}{e}$ and take $\frac{d^2\text{G}}{d\text{V}} = \frac{c}{e^2}\text{sech}^2\left(\frac{\text{V} - d}{e}\right)$.

The first integration gives

$$\frac{d\text{G}}{d\text{V}} = \frac{c}{e}\tanh\left(\frac{\text{V} - d}{e}\right) + b$$

and then a second integration gives

$$\text{G} = a + b\text{V} + c\ln\left(\cosh\left(\frac{\text{V} - d}{e}\right)\right).$$

The nonlinear least squares equation proposed for fitting the titration data is given by

$$y = a + bx + c\ln\left(\cosh\left(\frac{x - d}{e}\right)\right)$$

where:

a, b, c, e, d, are the nonlinear least-squares coefficients;

y is the model fitted y value, with y = G/μS and x = V/mL;

d is the calculated endpoint.

The iterative method started with initial estimates of the parameters. Successive improved values were calculated until the least-squares condition was satisfied. The initial parameters were estimated as follows:

d is the volume corresponding to half the difference between the final and initial gradients, $\frac{c}{e}$;

e is obtained by dividing the gradient value obtained above, $\frac{c}{e}$, by the estimated maximum curvature, $\frac{c}{e^2}$;

a, b, c are obtained by multiple linear regression using the equation $y = a + bx_1 + cx_2$;

where: $x_1 = \text{V/mL}$ and $x_2 = \ln\left(\cosh\left(\frac{\text{V/mL} - d}{e}\right)\right)$.

The model estimated end-point is used to calculate the base number of the sample using the equation $\text{BN} = \frac{d \times \text{M} \times 56.1}{\text{W}_{\text{oil}}}$.

3.8 Model Validation Techniques

Model validation is a procedure to assess the quality of a model. This is vital for both the development and functioning of the model.

Cross-validation (CV): is a technique used to asses the performance of a model. It is usually used to determine the number of significant components that characterise a data or the predictive ability of the model. CV is an extremely powerful method, due to its viability it is a standard procedure in multivariate analysis and integrated into most commercial software packages.

The basis of CV is to divide a data set into sub-groups so a portion of the data is kept out of the model development stage. The model is built on the reduced data and then tested on the omitted data. The cross-validated error is then calculated.

The error, known as the *predictive residual error sum of squares* (PRESS) is calculated.

$$\text{PRESS} = \sum \left(x_{ij} - {}^{cv}\hat{x}_{ij}\right)^2$$

This gives the sum of square difference between the calculated values and the actual values for each variable using the model.

There are several types of cross-validation available which are used according to applications. The common types are:

- **Leave-one-out cross-validation**: as the name suggests it involves using a single observation from the original dataset as the validation data, and the remaining observations as the training data. This is repeated such that each observation in the sample is used once as a validation data.
- **K-fold cross-validation:** the original sample is partitioned into K subsets, of the K subsets a single sample is retained as the validation data for testing the model while the remaining K-1 subsets are used as training data. The cross-validation process is repeated K times with each of the K subsets used exactly once as the validation data. The K results from the folds then can be averaged to produce a single estimation.

Test-Set: a test-set is an independent dataset used to evaluate the performance of the model. The model is developed on a set of data known as the training set, and then the model is used to predict the new dataset.

These mathematical/statistical procedures were employed to enhance problem-solving technique that contributes to understanding of lubricant degradation. The definitive aim of these methods is to help improve knowledge in the automotive lubricant research area.

Chapter 4

Results and Discussion

This chapter present results from the experimental investigations and their chemometric analyses. An initial part of this research involved the use of "data mining" techniques to extract implicit and useful information from top ring zone engine test datasets. The outcomes of these analyses and conclusions drawn have been published; titles are listed below with summaries. The significance of this work is of particular interest to mechanical/automotive engineers. The papers were directed towards such audience by publications in Proceedings of the **I MECH E Part D Journal of Automobile Engineering**.

4.1 Published Work

4.1.1 Correlation of field, laboratory and standard lubricant tests using multivariate analysis by Aruna M.A., Fox M.F. Proceedings of the I MECH E Part D Journal of Automobile Engineering, Volume 218, Number 2, February 2004, pp. 195-201(7)

The task of this study was to explore the dataset and establish the relationship between vehicle field test and laboratory engine test results. Lubricant samples were obtained from the engines of diesel and petrol vehicles after field trips, Petter W-1 petrol test engine and Castrol Saab Turbo test engine. The chemical/physical measurements performed on the lubricant samples, volatility test using a thermo gravimetric analyser (TGA), acid and base number determination and FTIR used to identify degradation products (carbonyl oxidation and nitration). Spectra showing degradation and contamination of used oil samples had been obtained by the method of "difference spectrum". This involved subtracting the spectrum of fresh oil from the absorbance spectra of used oil samples. The resulting difference was defined as the measurement of degradation products. The PCA and PLS models developed revealed relationships between the performance of the degraded samples obtained from the various test procedures.

4.1.2 Differentiation of lubricant degradation in the piston ring groove and crown land by multivariate data analysis by Aruna M.A., Fox M.F. Proceedings of the I MECH E Part D Journal of Automobile Engineering, Volume 218, Number 12, December 2004, pp. 1503-1511(9)

The objective of this analysis was to provide an insight into the relationship between the oil degradation and environmental conditions of the piston ring zone. Four formulated lubricants were tested at two sampling points on the Petter AA-1 diesel engine. The degree of oil degradation in the upper face region is believed to be higher than that observed in samples from the first ring groove. The PCA model developed using the degradation variable data (acquired by spectra subtraction) uncovered the relationship between the degraded lubricants in the ring zone area. The PLS-DA model showed discrimination between the formulated oils in terms of the oxidative/thermal stability of base oil and the additive properties of the lubricants. The oil degradation pattern featured in the PLS-DA scores and loadings plots suggested that the environmental conditions of the first ring groove distresses base oil performance while that of the upper face region degrade additive performance.

4.1.3 Differentiation between good, borderline and poor ASTM lubricant standards by ring zone sampling and multivariate data analysis by Aruna, MA; Datoo, A; Fox, M. Proceedings of the I MECH E Part D Journal of Automobile Engineering, Volume 220, Number 2, Febuary 2006, pp. 177-185(9)

The aim of this analysis was to investigate the performances of three formulated lubricants in the top ring zone region of a Petter W-1 petrol engine. The three lubricants were formulated to specific standards; to provide good, borderline and poor results from the engine test. PCA and PLS-DA model were developed on the degradation parameters obtained by FTIR spectra subtraction, thermo gravimetric analysis (TGA) and Viscosity measurement data. The PCA and PLS-DA scores and loadings plots provided detailed and visual insights about the degree of degradation and performance levels of the three formulations.

4.1.4 FTIR and multivariate data analysis approach for differentiation between good, borderline and poor ASTM lubricant standards by ring zone sampling by Aruna, M; Datoo, A; Fox, M. Poster Presentation at the 2005 Gordon Research Conference on Statistics in Chemistry and Chemical Engineering

Further work on the good to poor lubricants dataset involved using a PCA model to explore the FTIR spectral data of the oil samples. The outcome of the analysis showed that ample information can be obtained from investigating the whole FTIR spectrum. The suitability of PCA to analyse spectral data is a streamlined method compared to the "spectra subtraction" technique proposed by Coates and Setti[30-31] (routinely used by oil analysts) for characterisation of degradation products.

The technique definitely provides an optimised, efficient and feasible approach to lubricant oil condition monitoring with FTIR. Therefore subsequent analyses described in this chapter of this thesis were carried out using this procedure.

4.2 Base Number Measurement Results

The average base number results from three replicate conductimetric titrations performed on the lubricant oil samples are presented. The titration curves below illustrate the relationship between the conductance and addition of acid titrant to three samples of oil. The results illustrated below are typical of those obtained for severely degraded samples, degraded used oils and new lubricants.

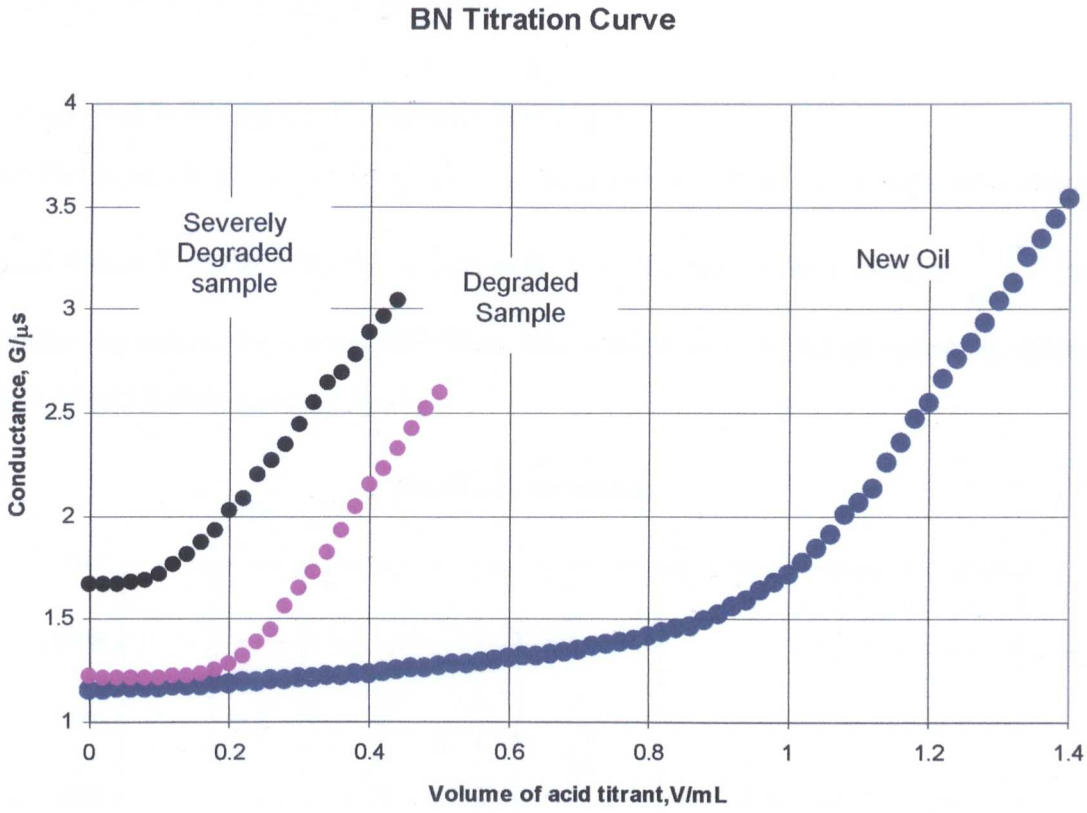


Figure 31: Base number titration curve for new, degraded and severely degraded lubricant samples

The visible differences between the samples relate to the quantity of base additive present in each sample. The conductance of the used oil samples rises much quicker than that of the new oil sample. It takes 0.1 mL and 0.2 mL of acid titrant to neutralise the alkaline component of the degraded samples, suggesting that there is very little alkali remaining, thus giving almost immediate rises in conductance due to excess acid accumulation. In comparison it takes much more acid titrant to completely neutralise the

alkaline content of the new oil. The distinctive conductivity response through the titration process facilitates endpoint evaluation and feasible computation of base number of the various lubricant oil samples.

The curve fitting methods described in Chapter 3 were used to estimate the titration endpoint and sequentially calculated base number for the oil samples. Taking the degraded sample shown in pink in Figure 31, the graphs below demonstrate how the calculations were performed on the titration data.

4.2.1 Method 1: Maximum Curvature (BN 1)

From the equation $y = a + bx + cx^2$ used to fit quadratic curves to the data, the volume of acid titrant V at the endpoint is estimated from the values for curvature $\frac{d^2y}{dx^2} = 2c$ calculated by taking the second derivative with respect to x. A plot of curvature values for the example data is shown below.

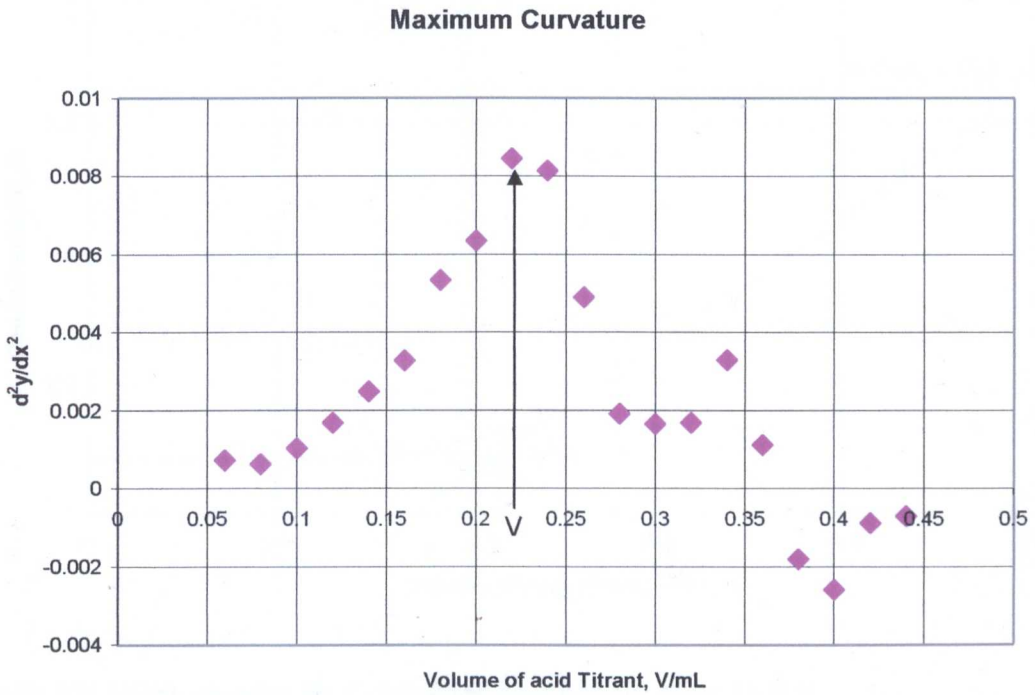


Figure 32: Plot of second derivative values used to estimate endpoint by method of maximum curvature

The endpoint is established as the volume at which the titration curve has maximum curvature. For the degraded sample the value is evident at 0.225 mL. The base number was then calculated using the equation

$$\text{BN} = \frac{0.225 \times 0.104 \times 56.1}{0.757} = 1.734$$

Hence method 1 suggests that the degraded sample of oil has a base number of 1.7 mg KOH/g.

4.2.2 Method 2: Least-squares Line Intersection (BN 2)

This method estimates the endpoint volume V by fitting two least-squares lines. The intersection of the two lines, illustrated in the plot below for the degraded sample shown in pink in Figure 31, gives the estimated endpoint volume V which is then used to determine the base number of the oil sample.

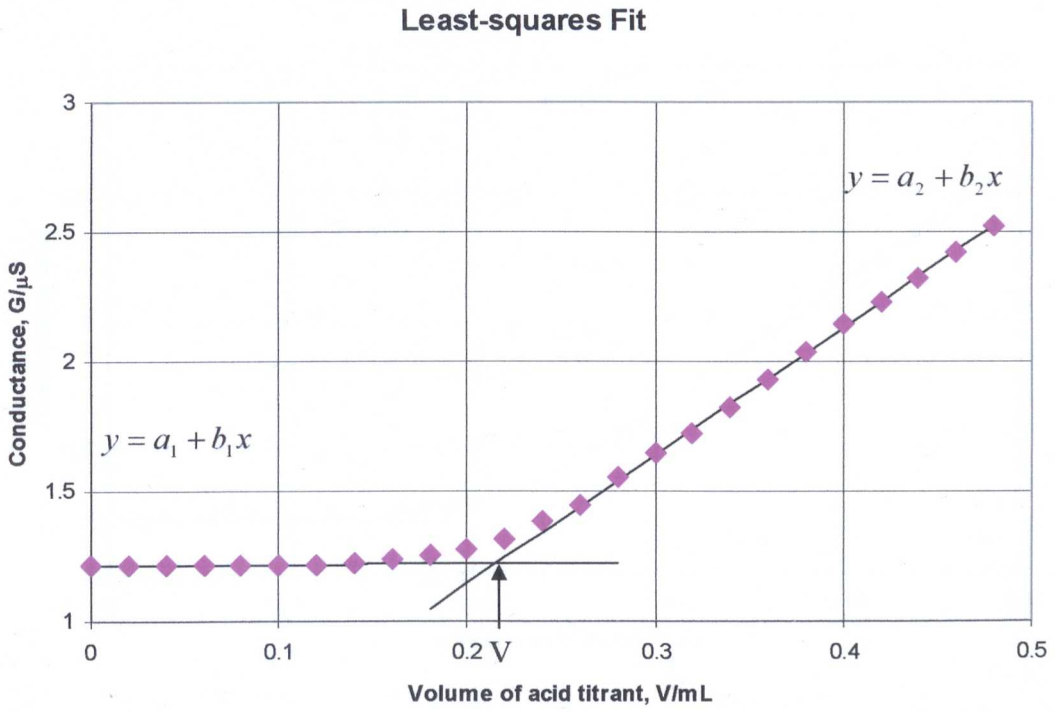


Figure 33: Least-squares fit to the base number titration curve

The endpoint volume, V, at the intersection is 0.22 mL for the degraded sample. Therefore the base number is

$$BN = \frac{0.22 \times 0.104 \times 56.1}{0.757} = 1.696$$

Method 2 also indicates a base number of 1.7 mg KOH/g for the degraded oil sample.

4.2.3 Method 3: Nonlinear Least-squares Fit (BN 3)

The nonlinear equation $y = a + bx + c\ln\left(\cosh\left(\frac{x-d}{e}\right)\right)$ is used in conjunction with the method of least-squares to fit the titration data. The parameter estimates that satisfied the least-squares condition for the degraded sample shown in pink in Figure 31 were established as $y = 0.773 + 2.492x + 0.134\ln\left(\cosh\left(\frac{x-0.216}{0.054}\right)\right)$. The fitted model is the line passing as close as possible to each point of the raw data in the graph below.

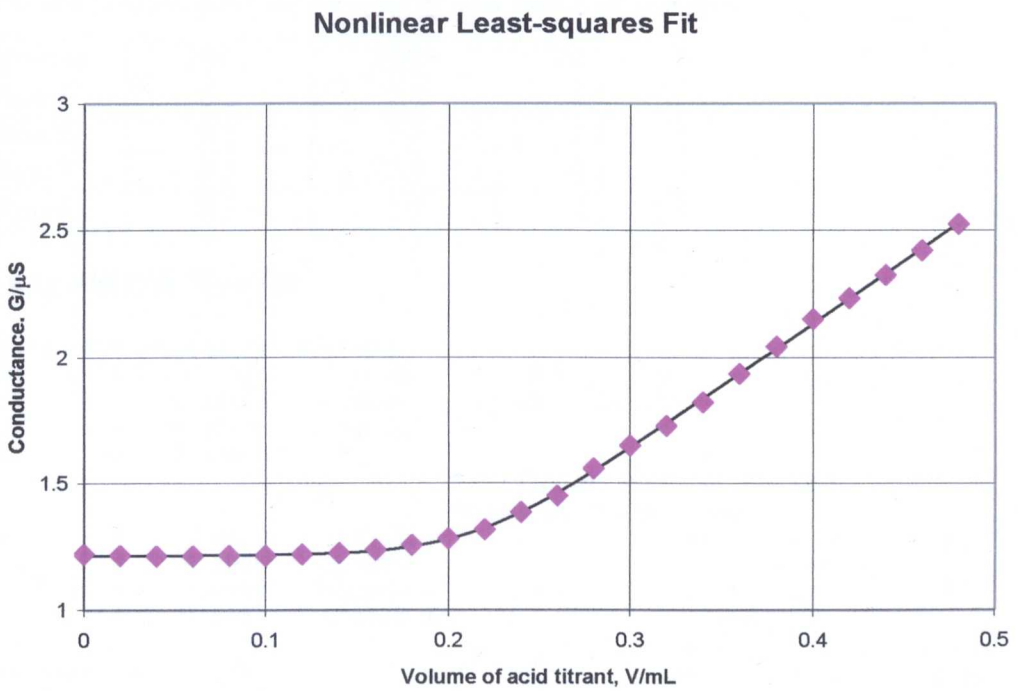


Figure 34: Nonlinear least-squares fit to base number titration curve

In the nonlinear equation the endpoint volume V is the value of d (0.216). Therefore the base number for the degraded sample was calculated as

$$BN = \frac{0.216 \times 0.104 \times 56.1}{0.757} = 1.665$$

Method 3 confirms the base number of the degraded sample as 1.7 mg KOH/g.

4.2.4 Analysis of variance

Although the principles of the three methods are different, very similar base number values were obtained for most of the oil samples. For a few samples, the three methods gave slightly different BN values. To test whether there was a significant difference between the three methods of calculation analysis of variance (ANOVA) was performed on some typical data. ANOVA was performed using MINITAB software.

Results are presented below for a set of new lubricant samples.

Titration	BN 1	BN 2	BN 3
Run 1	8.2	7.7	8.1
Run 2	8.2	7.7	8.1
Run 3	8.2	7.9	8.1
Run 4	8.3	7.7	8.1

One-way ANOVA: New Oil

```
Analysis of Variance for new oil
Source     DF        SS        MS        F        P
C5          2   0.38167   0.19083    31.23    0.000
Error       9   0.05500   0.00611
Total      11   0.43667

                                        Individual 95% CIs For Mean
                                        Based on Pooled StDev
Level      N      Mean     StDev  ------+---------+---------+---------+
BN 1       4    8.2000    0.0816                        (---*---)
BN 2       4    7.7750    0.0957  (----*---)
BN 3       4    8.0750    0.0500              (----*---)
                                  ------+---------+---------+---------+
Pooled StDev =   0.0782             7.80      8.00      8.20      8.40
```

The ANOVA output suggests that the means of the three methods are different. The F-statistic value and low P-value (probability) indicate there is a significant difference between the means of the BN methods 1, 2 and 3. The 95% confidence intervals for the average base number of the new oils estimated by the three methods are:

- for BN 1 between 8.10 and 8.26,

- BN 2 between 7.70 and 7.86,
- and BN 3 between 7.96 and 8.14.

These results are also illustrated in the box plot below.

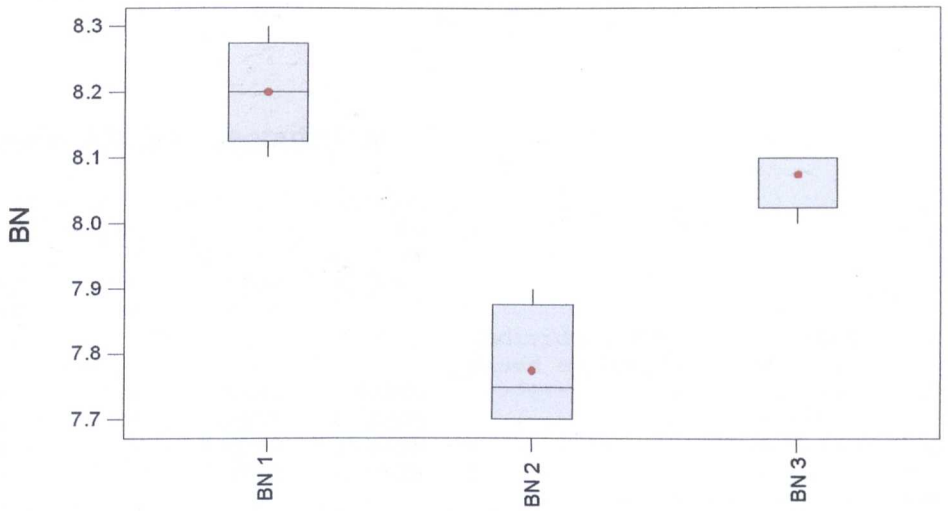


Figure 35: Boxplots for new oil samples

The boxplot provides a visual comparison of the location and variation of each BN method. The box stretches from the lower quartile (bottom of the plot) to the upper quartile (top of the box). The line across is the median and the red dot indicates the mean. The different range of each BN method relative to each other in the plot shows the difference between the calculated BN values for these oil samples. BN 1 gives the highest base number estimate while BN 2 provides the lowest estimates. The box of BN 3 method (which gives the closet fit to the data) lies between BN1 and BN 2, methods and only slight variation is observed within its output. The variation between the methods of calculation is greater for samples with higher base number. This is why there is a clear distinction with the new oil samples.

The results presented below were obtained by performing ANOVA on some typical severely degraded oil samples.

Titration	BN 1	BN 2	BN 3
Run 1	0.9	1.1	0.9
Run 2	0.9	0.9	0.9
Run 3	1.1	1.1	1.0

One-way ANOVA: Degraded Oil

```
Analysis of Variance for degraded oil
Source     DF        SS         MS         F         P
C11         2    0.0156     0.0078      0.78     0.501
Error       6    0.0600     0.0100
Total       8    0.0756

                                      Individual 95% CIs For Mean
                                      Based on Pooled StDev
Level      N      Mean      StDev   ----+---------+---------+---------+--
BN 1       3    0.9667     0.1155      (-----------*----------)
BN 2       3    1.0333     0.1155           (-----------*-----------)
BN 3       3    0.9333     0.0577   (-----------*-----------)
                                      ----+---------+---------+---------+--
Pooled StDev =   0.1000               0.84      0.96      1.08      1.20
```

The ANOVA result implies that there are no significant differences between the means of the three methods for this sample. Given the overlapping confidence intervals, very low F-value (0.78) and P-value of 0.501 the probability is extremely low for evidence to suggest a statistical difference. The 95% confidence interval show that the true BN value lies between 0.839 and 1.089 for BN 1, between 0.89 and 1.17 for BN 2, between 0.82 and 1.08 for BN 3.

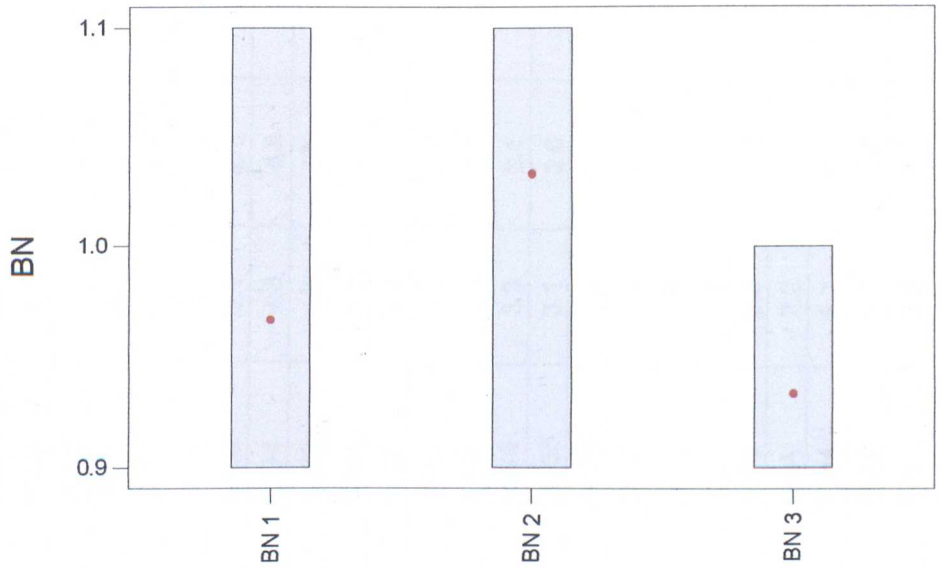


Figure 36: Boxplots for used oil sample

The plot shows the similarity between the methods; however the boxes for BN 1 and BN 2 suggest there is larger variation than occurs in the results from BN 3.

4.2.5 Sampling Exercise Results

Samples of new and used oils were obtained from multiple sources including work colleagues, friends, local garages and persons responding to an advertisement. Base number titrations were performed on each sample with between three and five replicates in every case. The analyses were carried out in randomised order to eliminate asmuch bias as possible.

Table 4 includes vehicle details, car and test mileage and the mean base number values determined by the three methods of calculation. An important aim was achieved by these results. There were no programme failures and all three methods gave meaningful results for ever titration. The actual experimental data recorded during these analyses are included on the data CD that is appended to this thesis. It is recommended that the interested reader should open the .SEQ files using Microsoft Excel.

Table 4: Base Number Results

Car used generally for short Journeys							
Sample Label	**Car Model**	**Engine Type**	**Car Mileage**	**Test Mileage**	**BN 1**	**BN 2**	**BN 3**
KF CAR 2	MERCEDES 190E	Petrol	116968	1000	8.2	8.0	8.2
DT	FIAT UNO	Petrol	74495	4780	6.6	6.3	6.9
KF CAR 1	BMW 520I	Petrol	17128	N/A	6.6	6.3	6.7
D CAR 5	VW POLO	Petrol	5350	5350	6.7	6.3	6.5
TT	PEUGEOT 405	Petrol	95832	N/A	5.3	5.0	5.2
DR	HONDA CIVIC	Petrol	97000	2000	5.1	5.0	5.0
TH	VW POLO	Petrol	3894	3894	4.8	4.8	4.8
RK	CITROEN C2	Petrol	7109	5869	4.4	4.1	4.4
CB	FORD FIESTA	Petrol	17576	3004	3.9	3.9	3.9
SL	VXH ZAFIRA	Petrol	28723	4026	3.8	3.7	3.8
PH	YARIS	Petrol	36131	6131	3.4	3.3	3.4
JS	MX5	Petrol	6449	3742	3.3	3.1	3.2
AB	SUBARU FORSTER	Petrol	62190	4294	3.3	3.1	3.2
CO	FORD FIESTA	Petrol	74955	14955	3.1	2.6	3.1
KH	VXH ZAFIRA	Petrol	34670	24670	3.2	3.2	3.1
KF CAR 3	TOYOTA COROLLA	Petrol	87189	6000	3.0	2.9	3.0
AR	MITSUBISHI	Petrol	85440	N/A	2.8	2.5	2.7
WH	ROVER 400	Petrol	70045	4492	2.6	2.4	2.5
SG	RENAULT RT	Petrol	102683	7683	2.2	1.9	2.2
WIT	DATSUN SUNNY	Petrol	62175	N/A	2.2	1.9	1.9
AS	VXH VECTRA	Diesel	21784	7784	8.7	8.0	8.8
DA	V W GOLF	Diesel	56906	1649	8.8	8.2	8.7
D CAR 6	FORD MONDEO	Diesel	45700	8700	8.8	8.7	8.6
D CAR 4	FORD MONDEO	Diesel	17700	5200	7.6	7.6	7.6

D CAR 1	FORD FOCUS	Diesel	12997	960	7.4	6.9	7.3
D CAR 2	LANDROVER DEFENDER	Diesel	14200	3100	7.2	6.7	7.1
NS	PEUGEOT 306	Diesel	121666	N/A	6.8	6.8	6.9
D CAR 3	FORD FOCUS	Diesel	11150	11150	6.9	6.5	6.8
PA	PEUGEOT 306	Diesel	61955	6000	6.5	6.0	6.4

4000 miles Oil Drain-Interval Garages							
Sample Label	**Car Model**	**Engine Type**	**Car Mileage**	**Test Mileage**	**BN 1**	**BN 2**	**BN 3**
SMG 1	RENAULT MEGANE	Petrol	156731	4713	6.4	5.9	6.4
SMG 3	FORD FOCUS	Petrol	17401	4001	4.9	4.8	4.9
SMG 2	FORD COURTINA	Petrol	82291	4000	4.4	4.3	4.3
SMG 7	ROVER METRO	Petrol	46606	5756	4.2	4.0	4.1
SMG 5	ROVER 214	Petrol	94986	5386	4.0	4.0	3.9
SMG 6	FORD MONDEO	Petrol	43908	4000	3.4	3.0	3.4
SMG 14	VW GOLF	Petrol	115300	6300	3.1	3.2	3.0
SMG 13	FORD FOCUS	Petrol	39916	7275	2.9	2.8	3.0
SMG 10	FORD MONDEO	Petrol	85471	11251	2.7	2.4	2.7
SMG 16	NISSAN MICRA	Petrol	102793	4895	2.6	2.2	2.6
SMG 17	NISSAN MICRA	Petrol	39384	5897	2.4	1.9	2.3
SMG 8	NISSAN PRIMERA	Petrol	82495	16522	2.1	2.1	2.1
SMG 15	NISSAN ALMERA TINO	Petrol	31966	6887	1.8	1.7	1.8
SMG 12	TOYOTA YARIS	Petrol	10779	10779	1.6	1.2	1.6
SMG 9	VXH ASTRA	Diesel	138430	3573	8.7	8.3	8.7
SMG 11	ROVER 420	Diesel	94034	3417	7.3	6.9	7.2
SMG 4	MITSHUBISHI	Diesel	27657	7640	6.3	6.0	6.3

GG	ROVER METRO	Petrol	70908	5908	3.4	3.3	3.3
SEAT1	Ibiza	Petrol	34500	4500	8.5	8.2	8.4
SEAT3	Ibiza	Petrol	16000	6000	4.2	4.1	4.2
SEAT2	Alhambra	Diesel	83050	3050	6.0	5.7	5.8
SEAT4	Leon	Diesel	42000	8000	5.5	5.3	5.5

9000 miles Oil Drain-Interval Garage							
Sample Label	**Car Model**	**Engine Type**	**Car Mileage**	**Test Mileage**	**BN 1**	**BN 2**	**BN 3**
MAZDA 2	RX 8	Petrol	12705	12705	7.7	7.4	7.6
MAZDA 9	RX 8	Petrol	33590	11708	6.6	6.3	6.7
MAZDA 10	RX 8	Petrol	25798	11959	5.8	5.5	5.9
MAZDA 6	RX 8	Petrol	38739	12716	4.9	4.6	4.8
MAZDA 12	RX 8	Petrol	7834	7834	4.5	4.3	4.6
MAZDA 13	RX 8	Petrol	13384	N/A	4.3	4.3	4.4
MAZDA 11	RX 8	Petrol	27368	14002	4.3	4.4	4.2
MAZDA 7	MX 5	Petrol	30885	14058	3.9	3.7	3.8
MAZDA 5	MX 5	Petrol	7317	7317	3.9	3.6	3.8
MAZDA 4	323	Petrol	17286	17286	3.4	3.4	3.4
MAZDA 8	MX 5	Petrol	2593	2593	3.3	3.4	3.2
MAZDA 3	121	Petrol	40175	3751	2.5	2.4	2.4
MAZDA 1	Premacy	Petrol	54050	6734	2.4	2.5	2.3

10000 to 13500 miles Oil Drain-Interval Garages							
Sample Label	**Car Model**	**Engine Type**	**Car Mileage**	**Test Mileage**	**BN 1**	**BN 2**	**BN 3**
FORD CAR 9	Mondeo	Petrol	51186	1186	8.6	8.3	8.6
FORD CAR 6	Focus	Petrol	33247	8247	5.7	5.5	5.7
FORD CAR 1	Focus	Petrol	16856	4356	5.6	5.3	5.5
FORD CAR 7	Mondeo	Diesel	58690	30	8.8	8.5	8.7
FORD CAR 8	Focus	Diesel	15971	1431	8.3	7.9	8.2
FORD CAR 5	Focus	Diesel	20333	7833	7.9	7.6	7.8
FORD CAR 2	Mondeo	Diesel	22205	9705	7.7	7.6	7.8
FORD CAR 3	Focus	Diesel	59962	9962	7.4	6.9	7.4
FORD CAR 4	Fiesta	Diesel	72490	9990	3.0	2.9	2.9
GEO CAR 1	VXH Vectra	Petrol	63124	10504	1.0	1.1	0.9
GEO CAR 2	VW Polo	Petrol	47651	14125	4.6	4.3	4.4
GEO CAR 3	Ford Mondeo	Petrol	75311	12811	3.5	3.5	3.4
GEO CAR 4	VW Polo	Petrol	78637	7263	3.7	3.5	3.6
MERCEDES 1	S320	Petrol	61274	11730	2.4	2.4	2.4
TOYOTA 1	Corolla	Petrol	2000	10050	1.9	1.6	1.8
TOYOTA 2	Corolla verso	Petrol	19962	10000	5.6	5.3	5.6
VOLVO 3	V40	Petrol	79331	1331	5.4	5	5.3
VOLVO 2	S40	Petrol	27808	3795	3.1	3.1	3.0
VOLVO 4	S40	Diesel	63841	15664	4.9	4.6	4.8
VOLVO 1	V40	Diesel	48764	12271	4.7	4.2	4.7
VAUXHALL 3	Vectra	Petrol	26949	8635	9.6	9.1	9.5

VAUXHALL 1	Astra	Petrol	39558		7.3	6.8	7.2
VAUXHALL 2	Astra	Petrol	70524	10000	3.4	3.3	3.4

20000 miles Oil Drain-Interval Garages							
Sample	**Car Model**	**Engine Type**	**Car Mileage**	**Test Mileage**	**BN 1**	**BN 2**	**BN 3**
AUDI 3	TT	Petrol	33405	14405	2.7	2.6	2.6
AUDI 1	A4	Diesel	23500	23500	7.8	7.5	7.6
AUDI 2	A6	Diesel	13200	13200	5.0	5.0	4.9
CITROEN 5	Xsara	Petrol	17468	8293	2.3	2.0	2.3
CITROEN 1	Xsara	Petrol	7720	7720	2.1	1.9	2.0
CITROEN 2	C5	Petrol	57292	17292	1.5	1.4	1.5
CITROEN 3	C5	Diesel	89669	14669	3.6	3.5	3.5
CITROEN 4	C5	Diesel	70583	20583	3.3	3.0	3.2
PEUGEOT 1	307	Petrol	40361	19904	3.2	3.3	3.0
PEUGEOT 2	307	Petrol	12827	12827	3.2	3.3	3.2
PEUGEOT 5	206	Diesel	24835	N/A	6.5	6.2	6.6
PEUGEOT 3	407	Diesel	41153	20955	6.4	6.1	6.4
PEUGEOT 4	406	Diesel	40646	20000	3.7	3.3	3.6

4.3 FTIR-ATR Experiment Results

All the lubricant oil samples collected from petrol and diesel engine vehicles described in Chapter 2 were analysed with the FTIR-ATR instrument, for each sample a spectrum was recorded. Due to the large number of data only a few spectra are shown here. The spectra obtained for all the samples are included in the data CD.

The subplots below were created using MATLAB 7 from the spectra data files produced by the Perkin Elmer FTIR/ATR instrument. The plots are used to illustrate variation by comparison between new and used lubricant samples.

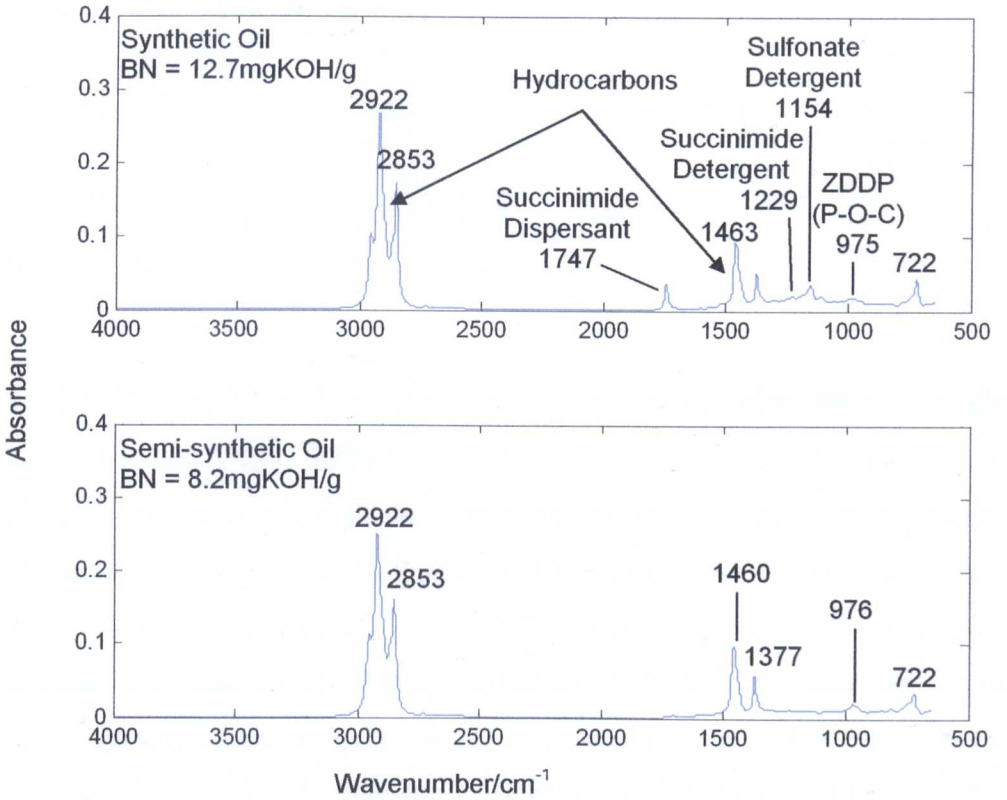


Figure 37: FTIR spectra of a semi-synthetic and synthetic new oil samples

The two spectra appear similar; however the fully synthetic oil has visible peaks at 1747 cm^{-1} and 1154 cm^{-1}. There is also slightly more absorbance at 950-1120 cm^{-1} which is related to the enhanced additive content in this oil as reflected in its high base number.

The subplot below shows the difference between new oil and a severely degraded petrol engine oil sample.

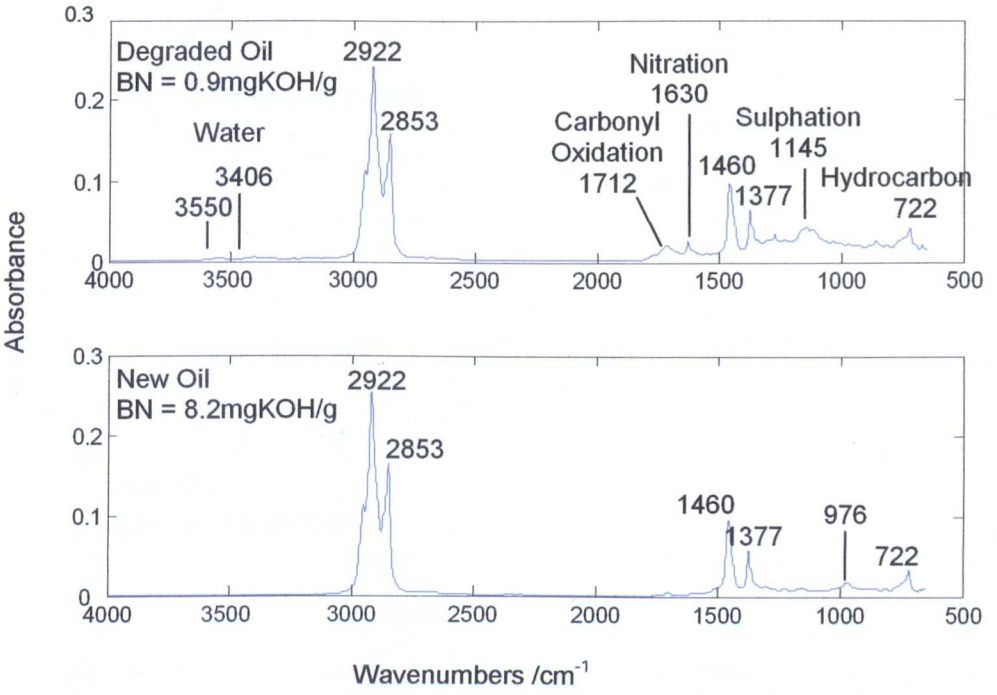


Figure 38: FTIR spectra of a new oil and a degraded petrol engine oil samples

These plots reveal visible differences between the two oil samples. In particular, the region between 1750 and 650 cm^{-1} indicates the presence of more components and higher background absorbance in the used oil compare to the new oil. Major differences are found in the 3600-3400 cm^{-1} and 1750-650 cm^{-1} regions of the spectrum. These differences are related to additive depletion, formation of degradation products involving oxidation, nitration, sulphation and contamination by water. This extensive degradation also explains the extremely low base number of the used oil sample.

The subplot below, Figure 39, illustrates the differences between new oil and a degraded diesel engine oil sample.

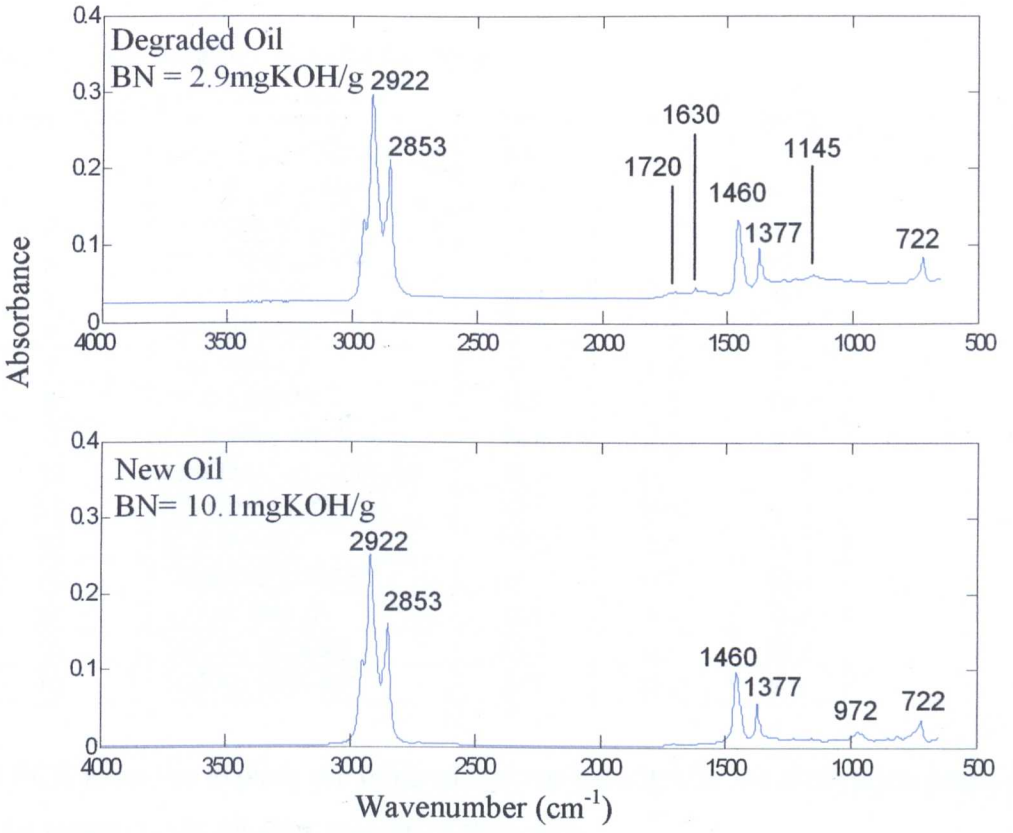


Figure 39: FTIR spectra of a new oil and degraded diesel oil sample.

The spectrum of the degraded diesel oil is distinctly different across the infrared spectrum to the corresponding new oil. The elevated baseline corresponds to high levels of carbon particulates in the sample. This is a characteristic of diesel engine oils; these particles cause a general scattering of the infrared radiation thus the significant shift in baseline. The degradation and contamination product in the oil is indicated by a slightly higher base line shift at 1800-650 cm^{-1} and the low base number value. The peaks at 1720, 1630 and 1145 cm^{-1} are due to carbonyl oxidation, nitrate and sulphate formation respectively.

4.3.1 PCA Model of New Lubricant Samples FTIR Spectra

The dataset consists of the FTIR-ATR spectra of the new lubricants. The initial base number analysis indicated the level of alkaline reserve in these lubricants.

Table 5: Base Number Results for New Oils

Sample Code	Sample	BN 1	BN 2	BN 3
1	CARLUBE 15W-40	10.9	10.8	11
2	CASTROL 10W40	8.2	7.8	8.2
3	COMMA 10W-40	8.2	7.8	8.2
4	ECO-TEC 0W-30	12.5	11.9	12.7
5	ELF 10W-40	8.3	8.2	8.4
6	EPS 20W-50	6.3	5.5	6.2
7	GM 10W-40	8.4	8.0	8.3
8	GTD 10W-40	10.2	9.8	10.3
9	GTX 10W-40	8.1	7.7	8.1
10	MAZDA DEX 10W-40	11.8	11.2	11.8
11	PD-DIESEL 5W-30	10.5	10.0	10.5
12	SLX 0W-30	10.3	9.8	10.3
13	TEXACO 10W-40	10.1	9.7	10.1
14	TOTAL 5W-30	9.4	8.8	9.3
15	TOTAL 10W-40	10.4	9.8	10.3
16	TOTAL 15W-40	9.9	10.0	9.9

The PCA aimed to explore the infrared spectra and identify the absorption peaks which can be related to the alkaline reserve of these oils.

A PCA model was developed using the FTIR-ATR spectra of the 16 new lubricant samples. The raw data matrix was first pre-processed by multiplying each column variable by the reciprocal of the square root of the standard deviation $\left(\frac{1}{\sqrt{stdev}}\right)$.

This form of scaling known as Pareto scaling without mean-centring was considered to be appropriate for these data as it gives each variable a variance numerically equal to its standard deviation. As a result the samples with distinctive absorbance peaks would be indicated.

The PCA model reduced the 16 by 3351 spectra data matrix into two orthogonal principal components which accounted for 99.8% of the variation in the data. PC 1 explains 98.8% and PC 2 describes 0.897% of the variation in the data. A scores plot of the first two PCs, which shows similarities and differences amongst the new lubricant oil samples, is shown below.

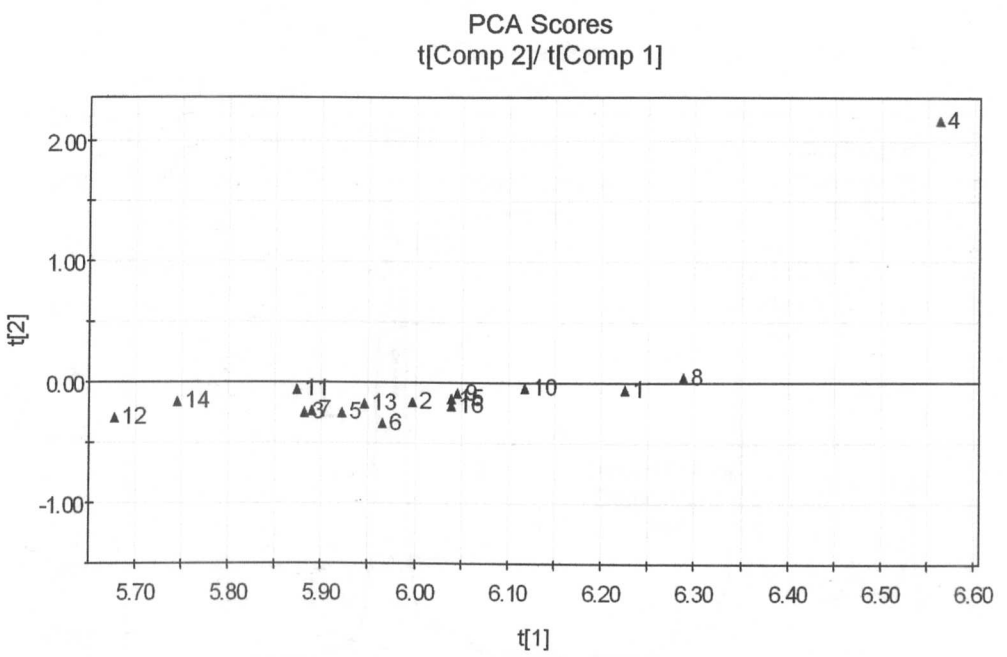


Figure 40: First two PC scores plot of new lubricant oil samples

The PCA scores plot (t_1, t_2) shows how the new oil samples vary. Overall the samples appear very similar with only little apparent difference amongst them. It is possible to classify the samples into three main groups with one outlier:

1. on the left hand side of the plot the synthetic oil samples, 12, 14, 11, (SLX-0W-30, TOT 5W-30 and PD-5W-30) appear separated from the rest of the samples;
2. the large cluster in the middle characterises the semi-synthetic oils;
3. while the diesel engine formulation oils,1 and 8, (CARL-15W-40 and GTD-10W-40) emerge slightly separated from the cluster on the right hand side.

The sample 4 (ECO-0W-30) is detached from the rest of the samples suggesting that it exhibits properties that might be different from the other lubricants. The loading plot is used to explain further the variation observed in this scores plot.

The loading plots below give an overview of the FTIR spectra. The loading plots show how the principal components are related to the absorbance at the 4000-650 cm^{-1} wavenumber. Each row of P^T (p_1 and p_2) can be interpreted as the spectrum that defines the observations in the scores plot.

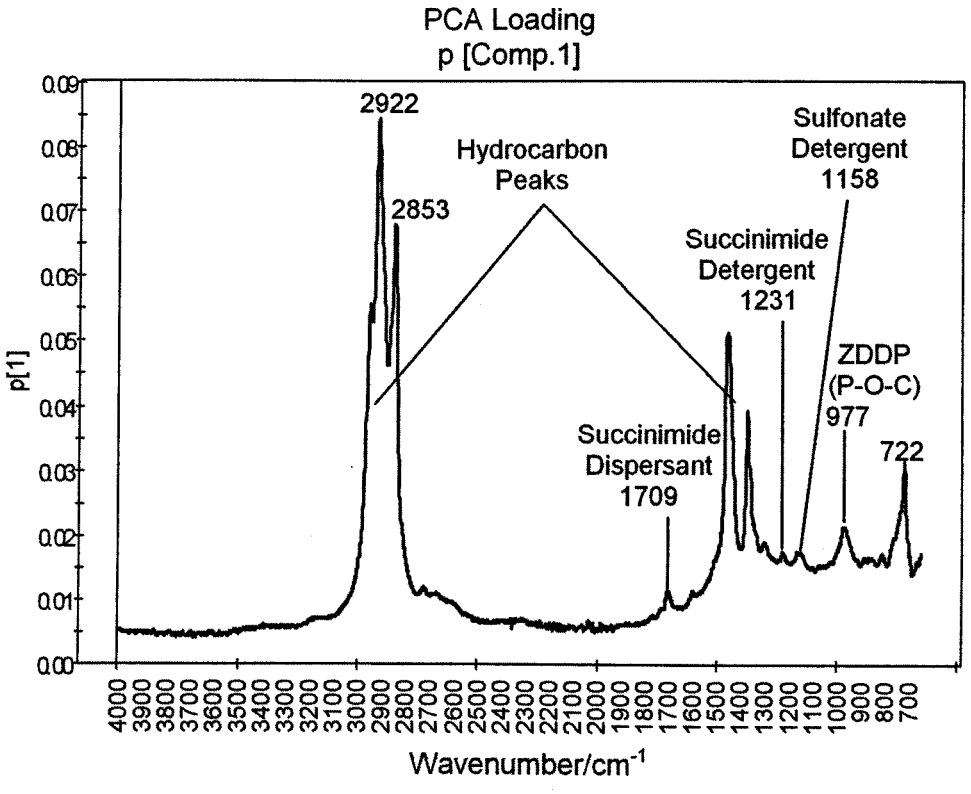


Figure 41: PC 1 loadings of new oil spectral data

The first principal component generally mirrors the weighted mean of the original spectra, hence information about the composition of the samples is provided. The peaks in this loading plot indicate the infrared absorption bands of the functional groups present in the new oil samples. The absorbance peaks that dominate the PC 1 plot are possibly the base oil components indicated by the hydrocarbon C-H stretching vibration at 3000-2800 cm^{-1} and bending 1490-1320 cm^{-1}; while the other evident peaks can be related to the variety of additive compounds, which are commonly included in the formulation of new lubricants to enhance the performance properties.

The second principal component, orthogonal to the first principal component provides information about predominant changes within the samples. The p_2 loading plot below shows the variation in the Infrared spectra of the new lubricant samples. The plot which includes positive and negative correlated absorbance peaks, relate to similar correlation in the scores plot in Figure 40.

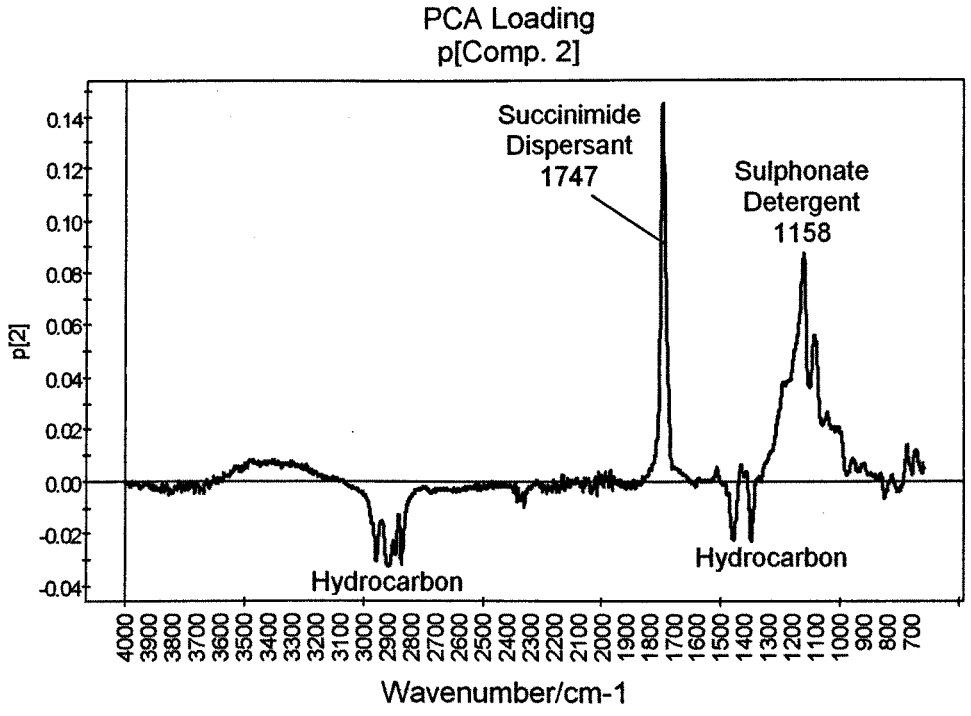


Figure 42: PC 2 loading of new oil spectra data

It appears that two main absorption peaks dominate the p_2 loading plot. These positively correlated peaks correspond to the sample named ECO-0W-30 (4) which appeared very different from the rest of the oils in the scores plot due to its highly positive weighting on t_2. The peaks are associated with the labelled additives, implying that this oil sample contains more of these additives.

From Chapter 1 we recall that detergent and dispersant additives contribute to the alkaline reserve of new lubricants. Since the base number measure for this sample (12.7 mg KOH/g) is also very high it is believed that the additive package is the main parameter which differentiates this sample from the other samples. To examine the details of the cluster in the score plot, the Eco-Tec sample was excluded and a new PCA model was developed.

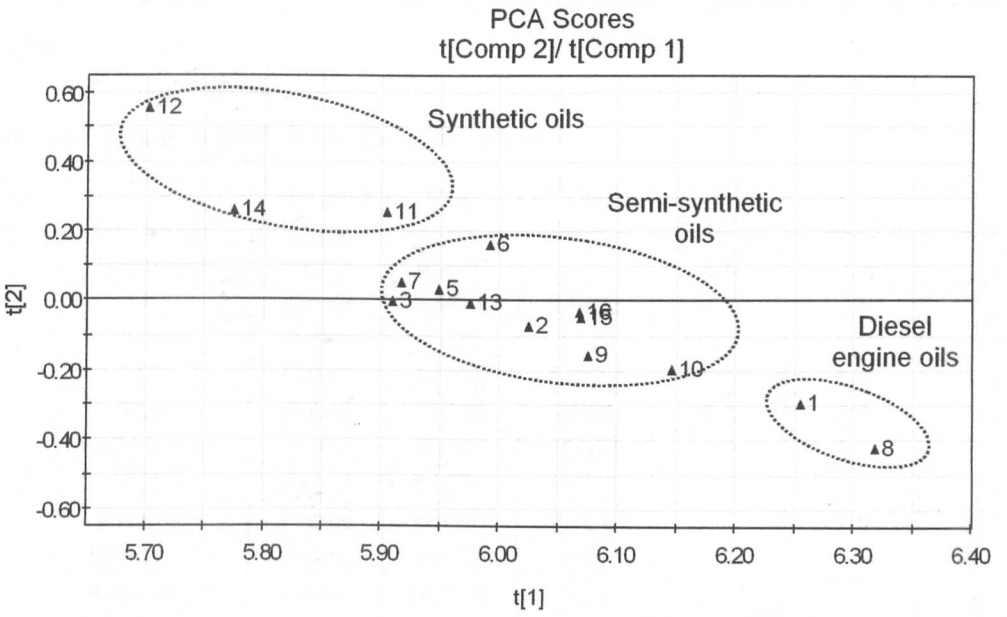


Figure 43: First two PC scores of the new PCA model for new oils

The new PCA score plot reveals better the variation within the samples with visible distinction between:

- the synthetic oils: formulated with specialised base stock and premium additives to give higher performance and extended drain intervals;
- the semi-synthetic: formulated with synthetic, mineral base stock and additives providing protection for moderate conditions;
- the diesel engine formulations: designed for use in diesel engines only.

This plots shows that the Eco-Tec sample had a significant effect on the first PCA model; however both models provide an objective overview into the new oil data with the loading plots revealing additive quality characteristic which differentiate them into synthetic, semi-synthetic and diesel engine oil formulations in the score plots.

Evidently the new oils have very similar chemical composition; this is due to the fact that all finished lubricants are generally formulated with the same primary components (i.e. base oils and additives). The resulting differentiation only reflects the variation in additive packages incorporated by different manufacturers to improve the performance properties of the lubricant.

4.3.2 PCA Model of Low Base Number oil Samples FTIR Spectra

This dataset contains the infrared spectra of the lubricant oil samples that have very low base number.

Table 6: Oil Samples with Low Base Number

Sample Code	Car Model	Engine Type	Car Mileage	Test Mileage	BN 1	BN 2	BN 3
1	Mitsubishi	Petrol	85440		2.8	2.5	2.7
2	TT	Petrol	33405	14405	2.7	2.6	2.6
3	Xsara	Petrol	7720	7720	2.1	1.9	2.0
4	C5	Petrol	57292	17292	1.5	1.4	1.5
5	Xsara	Petrol	17468	8293	2.3	2.0	2.3
6	VXH Vectra	petrol	63124	10504	1.0	1.1	0.9
7	S320	Petrol	61274	11730	2.4	2.4	2.4
8	Premacy	Petrol	54050	6734	2.4	2.5	2.3
9	Mazda 121	Petrol	40175	3751	2.5	2.4	2.4
10	Renault Rt	Petrol	102683	7683	2.2	1.9	2.2
11	Ford Mondeo	Petrol	85471	11251	2.7	2.4	2.7
12	Nissan Primera	Petrol	82495	16522	2.1	2.1	2.1
13	Toyota Yaris	Petrol	10779	10779	1.6	1.2	1.6
14	Nissan Almera	Petrol	31966	6887	1.8	1.7	1.8
15	Nissan micra	Petrol	102793	4895	2.6	2.2	2.6
16	Nissan micra	Petrol	39384	5897	2.4	1.9	2.3
17	Corolla	Petrol	2000	10050	1.9	1.6	1.8
18	Rover 400	Petrol	70045	4492	2.6	2.4	2.5
19	Datsun sunny	Petrol	62175	N/A	2.2	1.9	1.9

The aim of this analysis was to explore and characterise the absorption peaks that may be related to the degradative condition of these samples. A PCA model was developed on the pre-processed (Pareto scaled without mean-centring) FTIR-ATR spectra data. The first two PCs capture 99.7% of the data variation. The scores plot of PC 1 (98.4%) and PC 2 (1.25%) is given below.

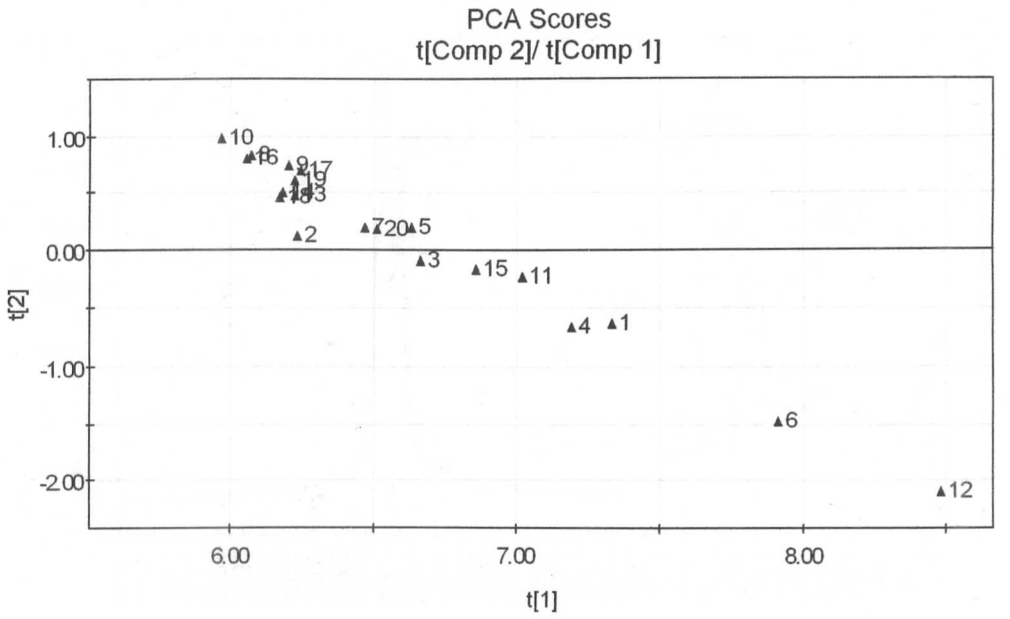


Figure 44: First two PC scores plot of low base number oil samples

The plot shows that within this dataset of low base number oils some samples are more degraded than others; thus the observed downward trend. The pattern follows a descending order from positive t_2 values to negative. Some observations lie remotely below the t_2 line, which implies that there are variations in the level of degradation within these samples. Oil samples with obvious discrepancy are those labelled, 6, and 12.

The loading plots give an overview of the spectrum for these low base number samples. The plots illustrate the peaks that characterise the samples in the scores plot. The plot of p_1 below that explains 98.4% of the variation shows the absorbance peaks that contribute to this estimate.

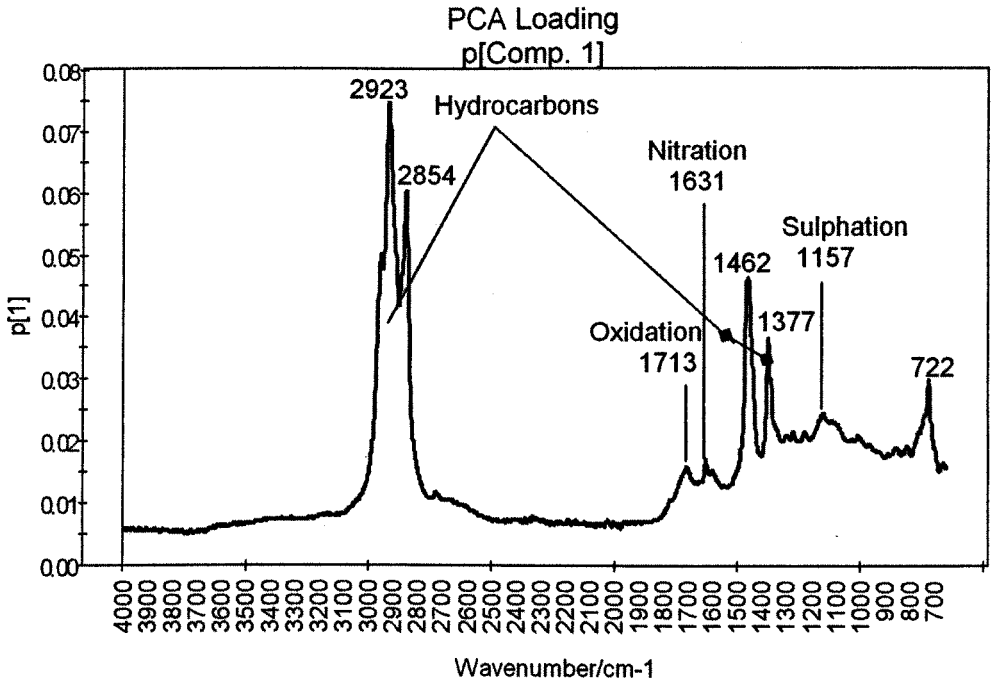


Figure 45: PC 1 loading plot of low base number samples

The absorbance peaks that dominate PC 1 are the hydrocarbons and absorbance that correspond to combustion by-products. The absorptions that signify degradation of the lubricant samples are the carbonyl oxidation, nitration and sulphation peaks. Aside from the hydrocarbon peaks these absorptions have significant contributions of the PC 1 model, indicating the severe conditions to which these lubricant samples have been subjected. The increase in base line below 1800 cm^{-1} is again apparent. It can be helpful to realise that the PC1 loading plot represents the average spectrum for the set of samples.

The remaining variation within the samples is explained by p_2. To facilitate comparison the plot of p_1 is also displayed. The p_2 loadings have positive and negative correlated peaks.

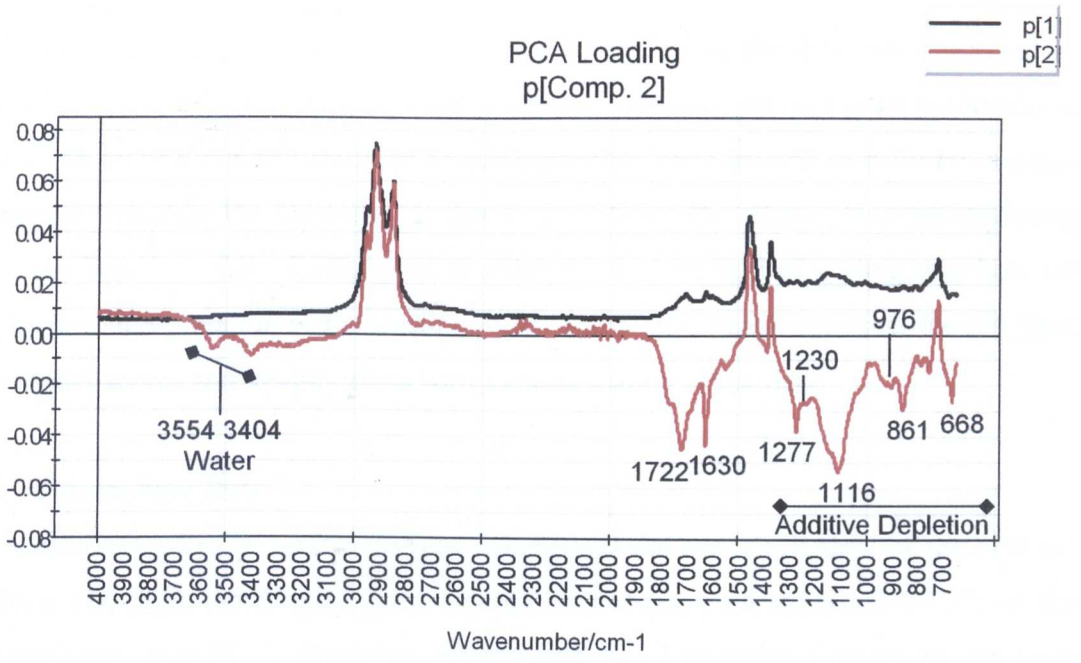


Figure 46: PC 1 and 2 loading plot of low base number samples

The p_2 plot reveals greater detail regarding the absorption. The absorbance peaks that are only just visible in p_1 are emphasized in p_2. Some samples appear contaminated by water, indicated on the left hand side. The negative absorbance peaks on the right of the graph signify depletion of additive components of the lubricants; this suggests that the oil samples in the scores which lie below the $t_2 = 0$ line are the most degraded samples with high levels of contaminants, combustion products with little or no additives left in the lubricants.

The two loading plots identify the absorptions that contribute to the degradative condition of these lubricant samples. The PCA model confirms the effectiveness of the base number analysis which initially indicated the severity of the degradation in these lubricant samples.

The unambiguous and easily interpretable loading plots are related to the quality of the raw spectra and the method of pre-processing prior to modelling. The Pareto scaling (without mean centring) contributes significantly to the clarity of the loading plots. The rationalization for the choice of scaling is disscused in the next section.

4.4 Scaling of Data

The importance of techniques of scaling prior to modelling the data was described in Chapter 3. Given the large datasets, it was necessary to scale the data prior to modelling in order to secure numeric stability of the algorithm; thus effects of different scaling techniques considered is illustrated in this section. Since the interest is in the deviation above the baseline of the FTIR spectrum, the choosen method of scaling was base on lucidity and interpretation of the loading plots. The graphs below illustrate the resultant PCA model scores and loading plots with various scaling of the data.

4.4.1 PCA on Raw Data

The application of PCA was performed initially on the raw FTIR data of the new oil samples. The PCA model performed directly on the raw data explained 99.9% of the data variation with PC 1 describing 99.8% and PC 2 provides 0.141% of the total variance. The variation within the lubricant samples is shown in the scores plot below.

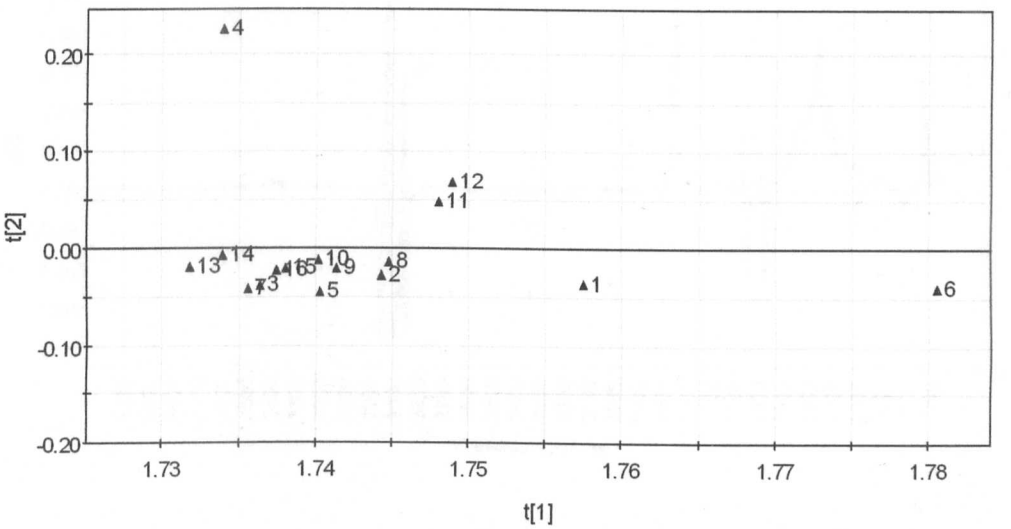


Figure 47: First two PC scores plot of the raw data

The main features of the plot suggest that two samples of oil, 4, (Eco-Tec 0W-30) and 6 (EPS 20W-50) have clearly different properties from the other oils. They lie far from the other samples; Eco-Tec 0W-30 has the highest weighting on t_2 and EPS 20W-50 has the highest on t_1. Samples with closely related properties form a cluster at the centre of the plot.

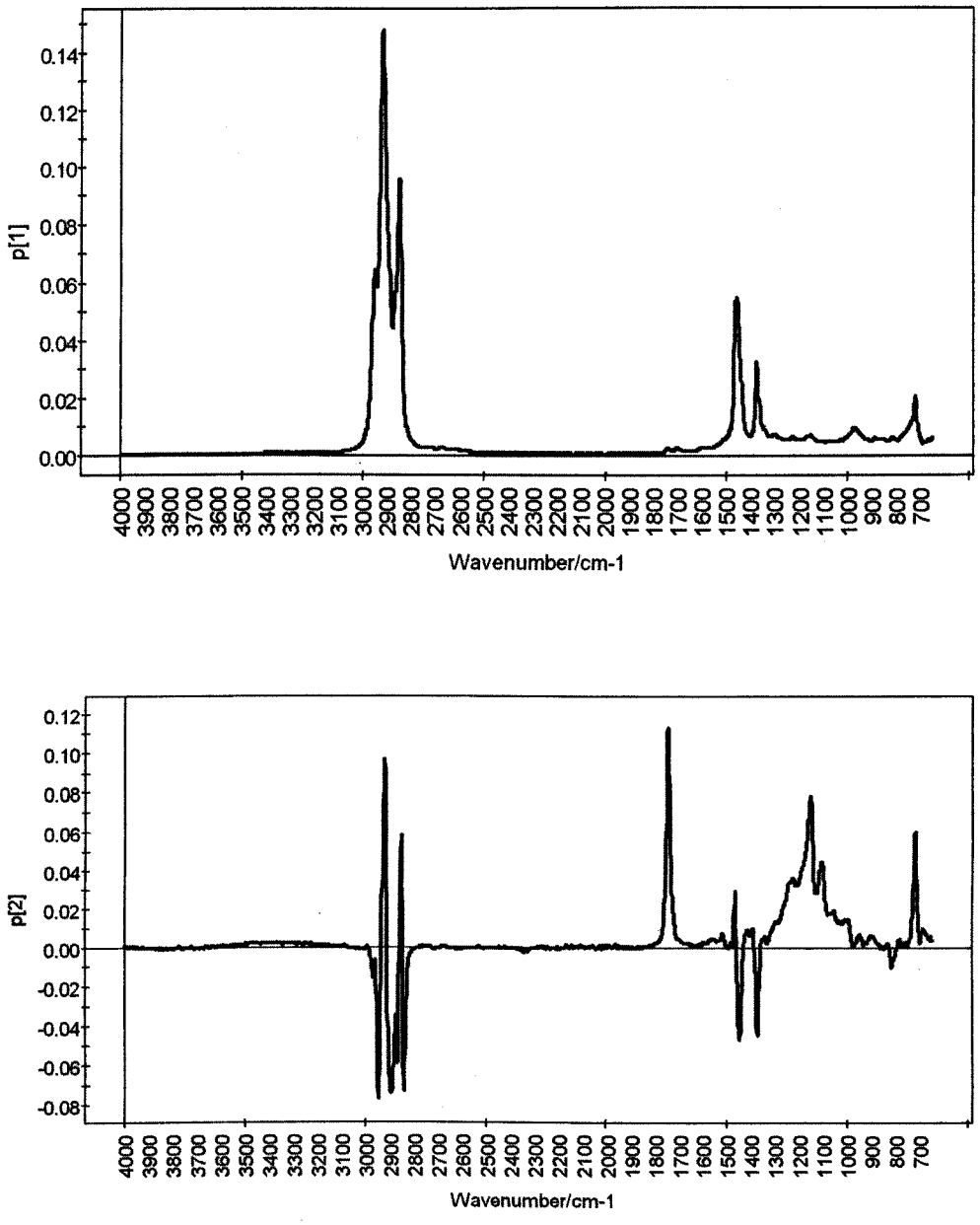


Figure 48: First two PC loading plots of the No scaling data

The p_1 loading is reminiscent of the raw FTIR spectrum; the region of common interest (i.e. 1800 to 650 cm^{-1}) appears subtle. However p_2 reveals that there are significant absorptions between 1800 and 700 cm^{-1} of the spectrum which can be associated with differences in the scores plot.

4.4.2 PCA on Mean-centred Data

The variables of the dataset are mean-centred by subtracting each observation from its column mean so the sum of the column is zero. PCA performed on this scaled data describe 88.3% of the variation; PC 1 accounts for 56.9% and PC 2 explains 31.5% of the total variation. Below are the resulting PCA model scores and loading plots.

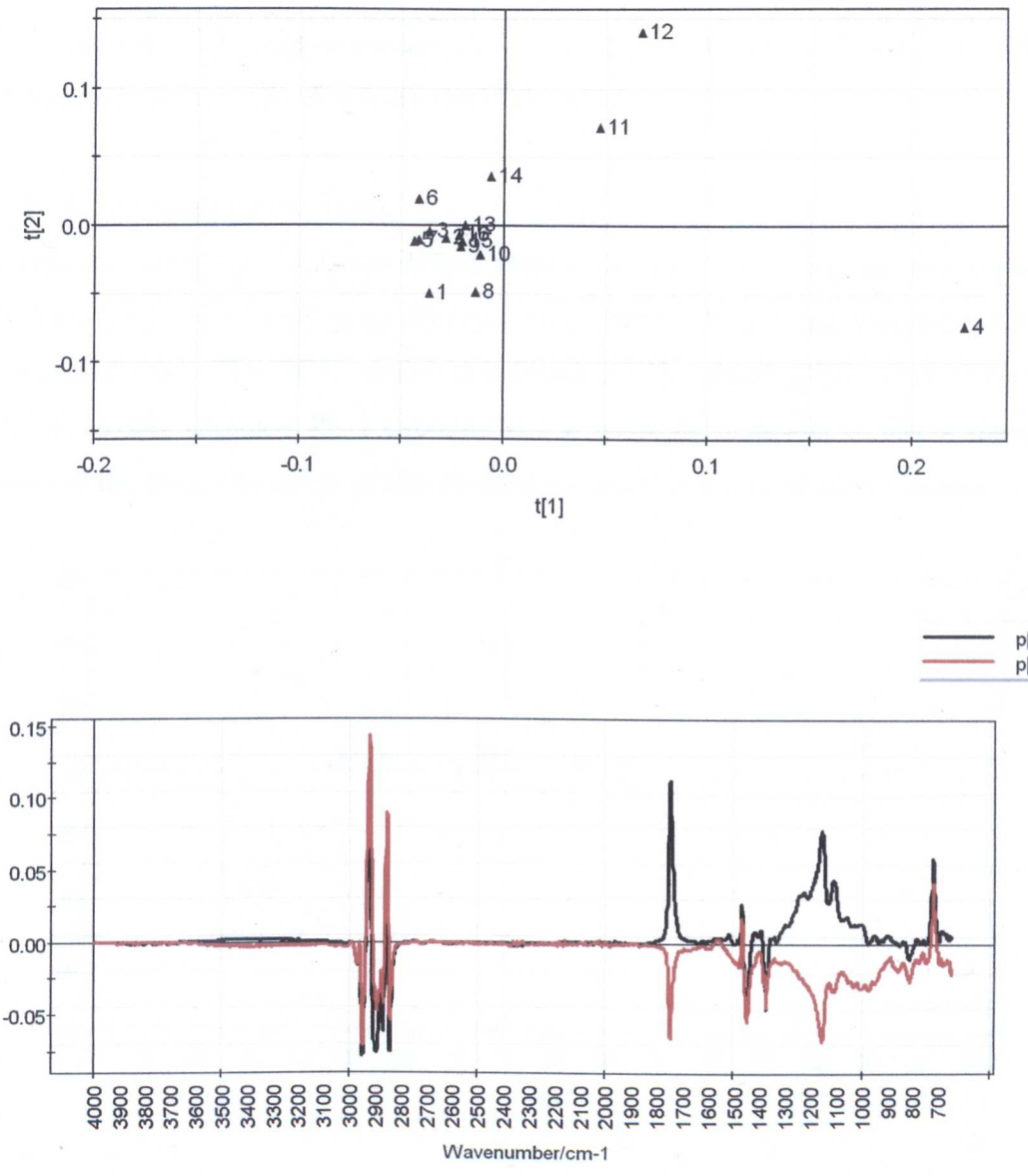


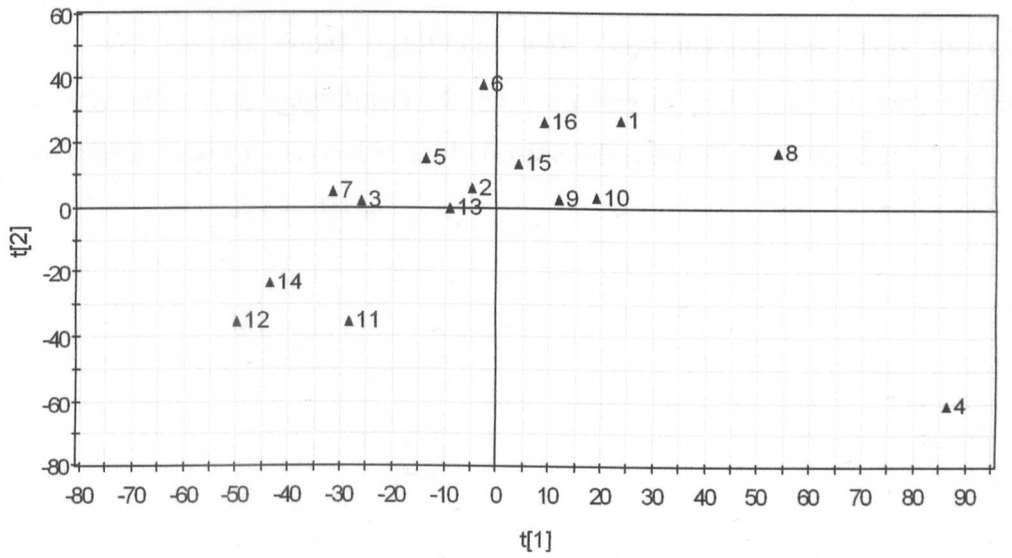
Figure 49: First two PC scores and loading plots of the mean-centred data

Both graphs have changed slightly, the main difference in the scores plot being that observations are centred on the origin. The first PC loading is identical to PC 2 of the

previous model. However the peaks in p_2 are negative, because when the positive contribution of the first PC is removed the remaining contribution will be negative since the weighted average is zero. This form of scaling is appropriate for variables with the same unit (e.g. spectroscopy). The method assumes that variables with large variation (high absorbance) are important. However it was inappropriate in this work, particularly in used oil spectra, where the hydrocarbon peaks inherently have larger variation due to their characteristic high absorbance at 2850-3000 cm^{-1} and 1350-1470 cm^{-1}. Therefore these regions automatically dominate the PCA model.

4.4.3 PCA on Standardised Data

This method suppresses variation effect within the data by scaling to unit variance (UV). Each variable is divided by its standard deviation, and in addition the data are also mean-centred. The PCA model developed on the standardised data described 58.1% of the data variance; PC 1 explains 37.2% while PC 2 details 20.9% of the total variation in the data. The effect of this method on the PCA model is shown below.



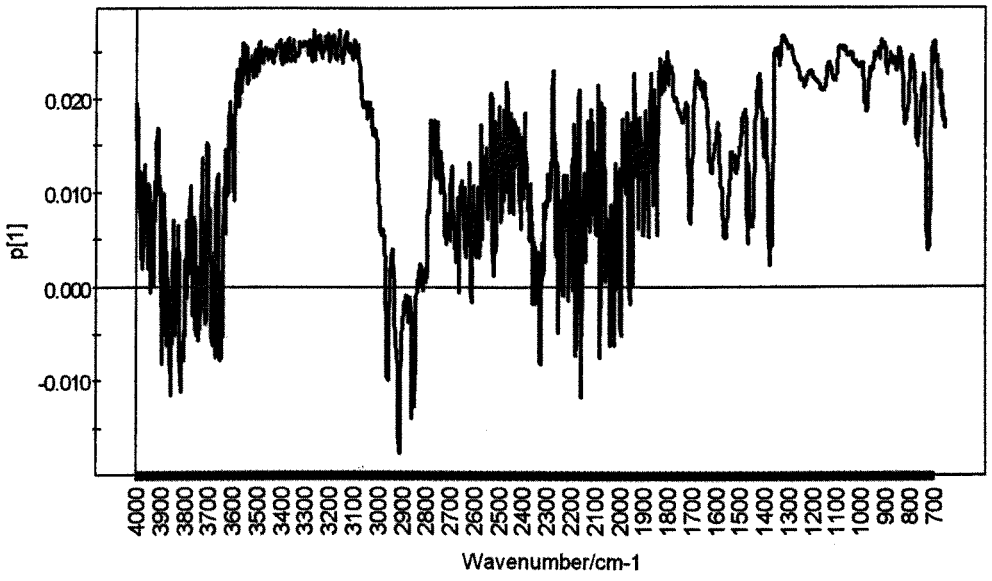


Figure 50: First two PC scores and PC 1 loading plot of the UV-scaled data

The scores plot is slightly different but there is a dramatic effect in the appearance of the loading plot. This is because the all variables have an equal weighting; as a result low absorbance will assume equal significant with high absorbances. This method is practical only when the magnitudes of the variables in a dataset are very different. Therefore standardisation was not suitable for the lubricant oil FTIR spectral data.

4.5 Trend Analysis

The experimental results from the time series set of samples collected from the Honda 1.8 petrol engine, the Peugeot 1.9 diesel engine and Castrol diesel engine sump test are presented in this section.

4.5.1 Honda 1.8 Petrol engine

4.5.1.1 Base Number Results and Trend Analysis

The table below displays the base number measurement results for the petrol engine oil samples. Each base number value represents the mean of three titration analyses.

Table 7: Base Number Result for Petrol Engine Oils

Sample	Date	Car mileage	Oil Test Mileage	BN 1	BN 2	BN 3
GTX	27/06/2005	51547	0	8.1	7.7	8.1
USP 1	21/07/2005	52107	560	7.1	6.7	7.0
USP 2	30/08/2005	52360	813	6.2	6.0	6.3
USP 3	25/09/2005	52978	1431	5.8	5.4	5.8
USP 4	22/10/2005	53717	2170	5.0	4.6	5.1
USP 5	30/10/2005	53753	2206	4.9	4.5	4.9
USP 6	26/11/2005	54533	2986	4.0	3.8	3.9
USP 7	14/12/2005	55034	3487	3.4	3.2	3.3
USP 8	25/01/2006	56061	4514	2.8	2.5	2.7
USP 9	27/03/2006	56802	5255	2.9	2.7	2.8
USP 10	19/04/2006	58074	6527	2.7	2.5	2.7
USP 11	14/05/2006	58660	7113	2.4	2.2	2.5
USP 12	31/05/2006	59070	7523	2.5	2.1	2.5
USP 13	23/06/2006	59652	8105	2.6	2.3	2.5

Details of the petrol engine samples are given in the table, the base number values were calculated by the methods of linear and nonlinear least squares described in Chapter 3. A plot of base number values against the oil mileage shown below gives an overview of the base number trend.

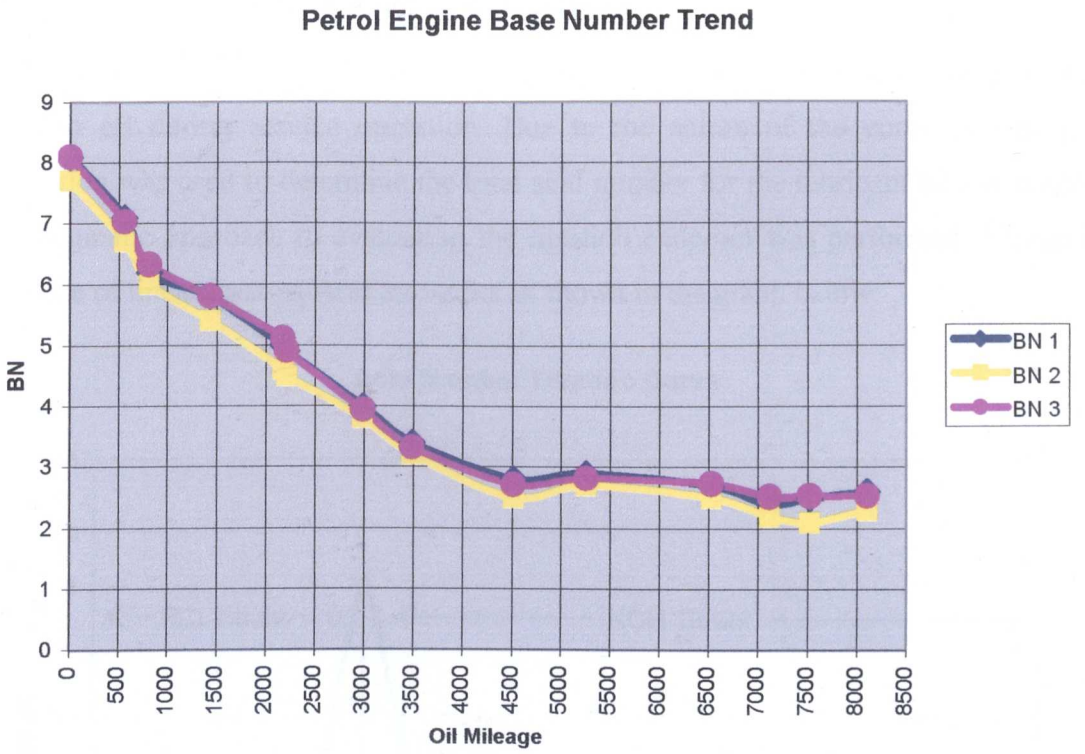


Figure 51: Base number against oil mileage plot for petrol engine samples

The BN values calculated using the three curve fitting methods are illustrated in the plot. In general the three BN outputs have similar downward trends, BN 2 the linear least-squares estimate provides lower values, BN 1, method of maximum curvature presents higher values while BN 3, the nonlinear least-squares method which is the closest fit to the data lies between methods 1 and 2.

The oil samples were collected and analysed over a year, consequently the lubricating oil endured various weather conditions which began in summer, progressed through autumn, winter, spring and finally completing its service in the summer.

From the new oil at 8.2 mg KOH/g a slow drop in the BN values is observed between the first three samples. Just before 1000 miles the values start to fall rapidly until 4500 miles where it appears slightly elevated before another drop after 6500 miles. The cycle approaches the end with a steady BN reading at 2.5 mg KOH/g for the last 3 samples.

This vehicle has negligible oil consumption and no fresh new oil was added during the test.

4.5.1.2 Acid Number Results and Trend Analysis

Acid number titration was performed to study the build up of acid products in the lubricant oil during service operation. Due to the nature of the curve a multipart calculation was used to determine the total acid number for the lubricant oils. A simple and pragmatic approach to evaluating the titration endpoint was performed through a sequence of linear least-squares curve fits as shown in the graph below.

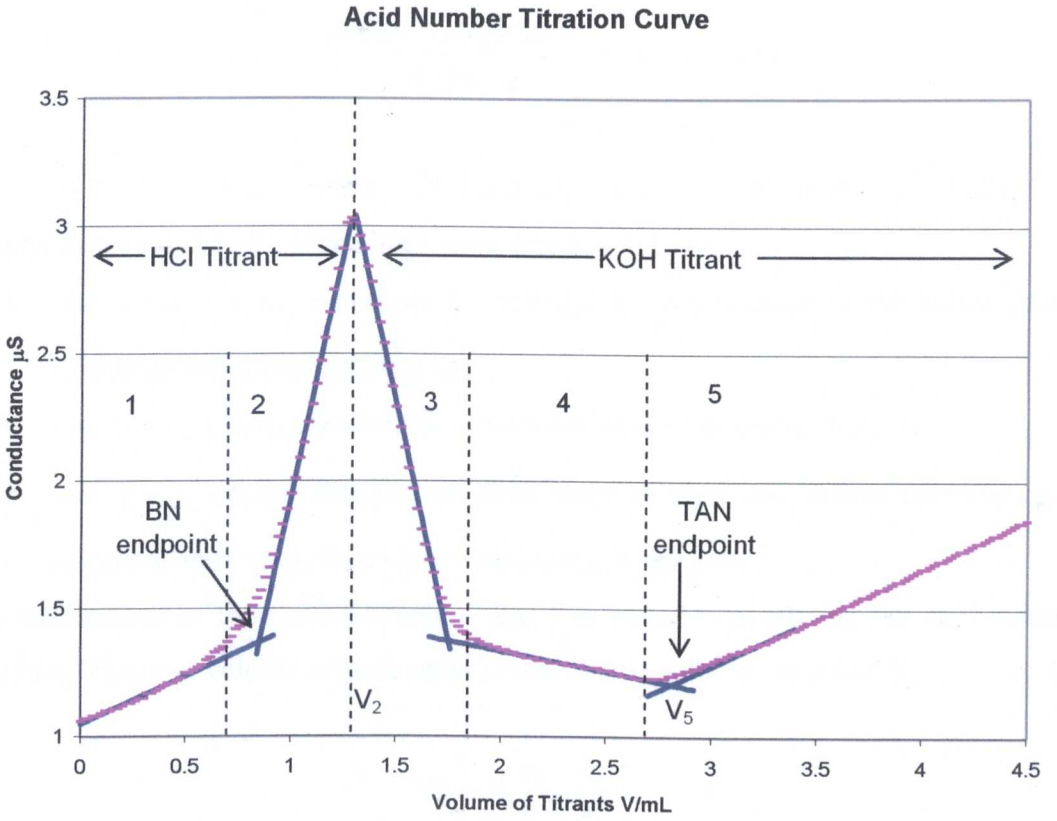


Figure 52: Least-squares fit to the acid number back titration curve

Five least-squares lines were required for the AN endpoint estimation which was then used to calculate the total acid number of the sample. The calculations were performed using the Microsoft Excel software, the dataset was colour coded into five regions, of which a least-square line was fitted using the "LINEST" function as described below;

Stage 1 and 2 of the plot illustrate neutralisation of the alkali content of the oil sample by addition of alcoholic hydrochloric acid titrant (i.e. base number) this stage required two lines:

1. the initial line $y = a_1 + b_1 x_{(1)}$ used to fit stage 1 (acid neutralisation);
2. the second line $y = a_2 + b_2 x_{(2)}$ used to fit stage 2 (excess acid).

The intersection of these two lines $V_1 = -\left(\frac{a_2 - a_1}{b_2 - b_1}\right)$ is used to estimate the base number titration endpoint which was subsequently used to calculate the base number. For this oil sample V_1 = 0.852 mL and so

$$BN = \frac{0.852 \times 0.104 \times 56.1}{0.718} = 6.92 \text{ mg KOH/g}$$

Stages 3, 4 and 5 relate to the back titration; addition of KOH neutralises the acid content of the oil sample. Three lines were fitted as follows:

3. line $y = a_3 + b_3 x_{(3)}$ was fitted to the stage 3, neutralisation of the excess strong acid from the preceding titration;
4. line $y = a_4 + b_4 x_{(4)}$ continuous reaction of base with acidic species;
5. line $y = a_5 + b_5 x_{(5)}$ fitted to the final stage of the curve, where the titration is complete and excess KOH is accumulating in solution.

The intersection of the lines between 4 and 5 is used in calculating the acid number endpoint. The total volume of both titrants used at this point is estimated by

$$V_5 = -\left(\frac{a_5 - a_4}{b_5 - b_4}\right)$$

This volume is then used to calculate the acid number using the equation below

$$TAN = \frac{\left(V_5 - V_2\left(1 + \frac{c_A}{c_B}\right)\right) \times 56.1 \times c_B}{W_{oil}}$$

where:

V_5 = final endpoint volume;

V_2 = total volume of HCl used;

c_A and c_B = concentration of HCl and KOH titrants;

W_{oil} = mass of oil sample.

For the sample used to illustrate this calculation $V_5 = 2.816$ mL and $V_2 = 1.26$ mL

$$\therefore \text{TAN}_{(\text{USP1})} = \frac{\left(2.816 - 1.26\left(1 + \frac{0.104}{0.089}\right)\right) \times 56.1 \times 0.089}{0.718} = 0.582 \text{ mg KOH/g}$$

The total acid number values for each of the petrol engine oil samples were determined using calculations similar to the example above. The results are presented in the table below.

Table 8: Acid Number Result for Petrol Engine Oil Samples

Date	Oil Mileage	Time/days	BN	TAN	TAN + BN
27/06/2005	0	0	8.5	2.1	10.6
21/07/2005	560	24	6.9	0.6	7.5
30/08/2005	813	64	6.1	0.7	6.8
25/09/2005	1431	90	5.3	1.3	6.6
22/10/2005	2170	117	4.7	1.3	6.1
30/10/2005	2206	125	4.5	1.5	6.0
26/11/2005	2986	152	3.4	1.6	5.1
14/12/2005	3487	170	2.9	2.4	5.4
25/01/2006	4514	212	2.7	2.9	5.6
27/03/2006	5255	273	2.6	3.0	5.6
19/04/2006	6527	296	2.5	3.1	5.6
14/05/2006	7113	321	2.5	3.2	5.7
31/05/2006	7523	338	2.3	3.3	5.6
23/06/2006	8105	361	2.2	3.7	5.9

The table shows the acid number values for the entire set of lubricant oil samples. In addition the base number values obtained from the first stage of the back titration are included, oil mileage, sample date and corresponding elapsed time in days and the sum

of the acid and base number values. A plot of the acid number values against oil mileage is shown below.

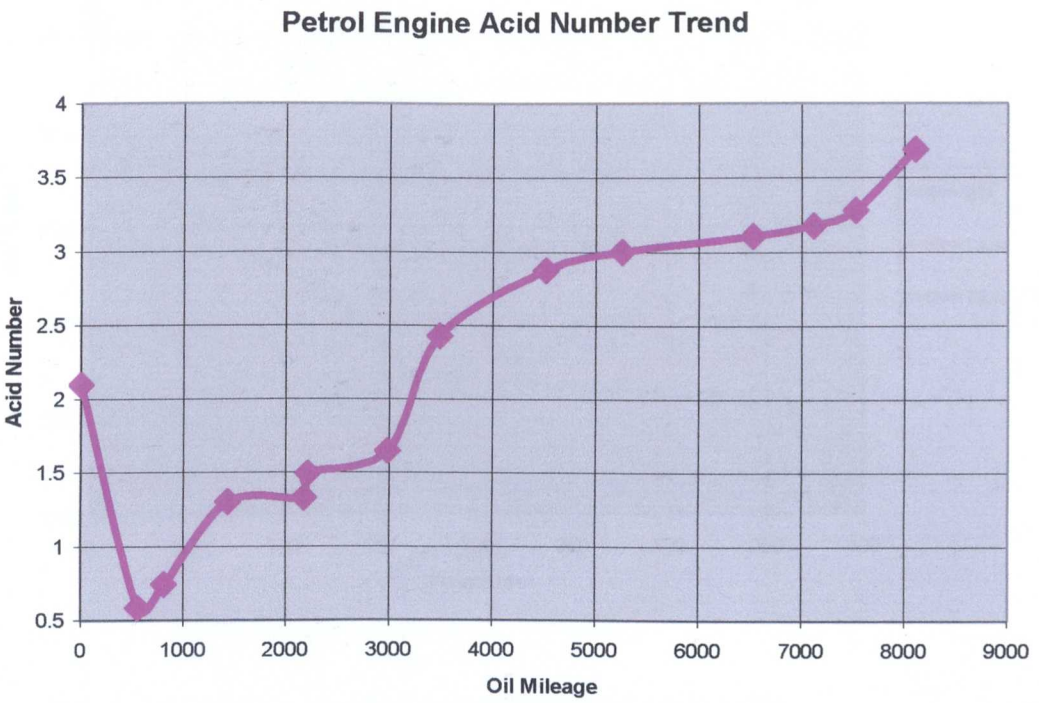


Figure 53: Acid number against oil mileage plot for petrol engine samples

The plot reveals an unexpected decline in acid number, with a preliminary value of 2.1 mg KOH/g in the new oil to 0.6 mg KOH/g of the initial 560 oil mileage. The first rise is observed after 813 miles, a noticeable second rise appears after 3000 miles, before the final increase of the last 500 miles. In general the build up of acid products grows with increasing mileage. However the existence of a significantly high acid number in the new oil can only be associated with properties that have not been disclosed by the manufacturer.

A plot facilitating a comparison of the results from acid and base number measurements is shown below.

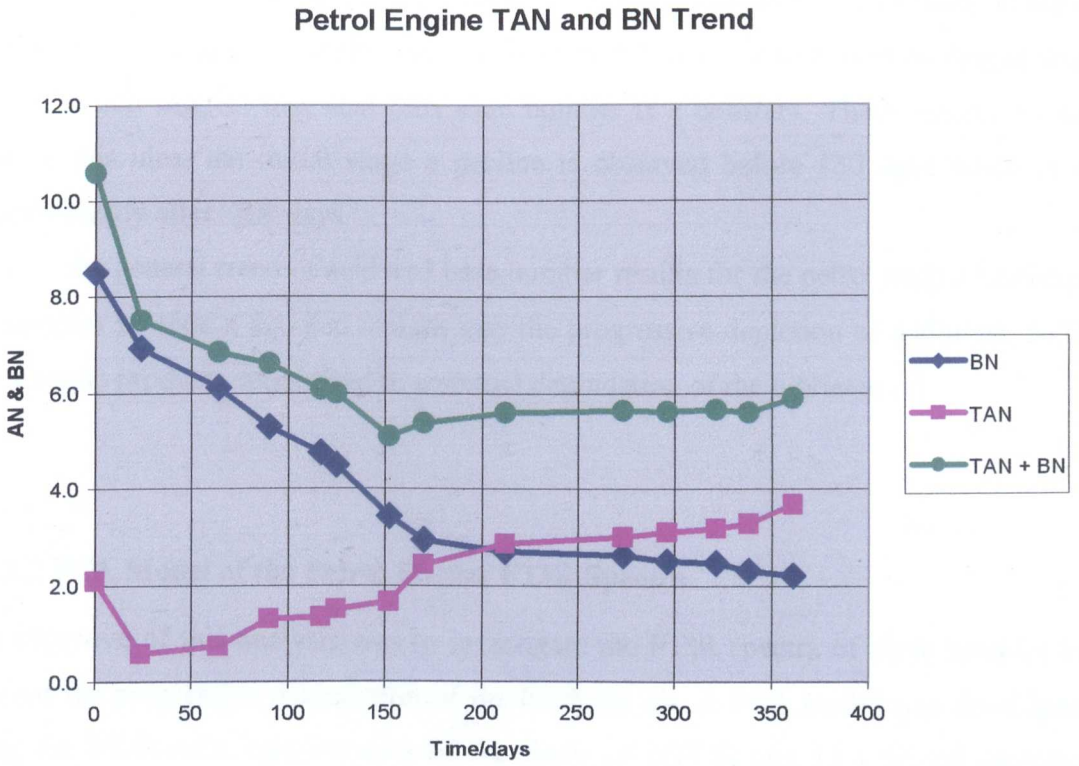


Figure 54: Acid and base number trend for petrol engine oils

The results show that the decline in base number corresponds to an increase in acid number. The relationship between the acid and base number curves can be interpreted as follows.

- Before the intersection of the two curves, outline of the TAN and BN curves show the oil deteriorates considerably within the first 200 days. The oil mileage at this point (4514 miles), proves the vehicle had done over half its total year mileage. These suggest that at an early stage of the lubricant's use, the oil alkaline reserve are predominantly utilised while the degradation products are formed. However this period also corresponds to the wintry season of the year signifying that weather and temperature may be a causal factor affecting the oxidative and thermal stability of the lubricant oil;
- The later part (after 200 days) shows relatively steady increase in acid number and decrease in base number. This stage shows the effect of prolonged oxidation as accumulation of acid products and exhaustion of alkaline reserves in the lubricant progress, towards the end of its service use.

The curve above the acid and base number curves is the sum of the two values. There is an empirical concept, not based on any theoretical work, usually used in degradation studies which suggest that acid plus base number is a constant. These results do not support this idea, the initial stage a decline is observed before 150 days however it appears steady after 200 days.

The general trend of acid and base number results for the petrol engine lubricant oil samples provide a detailed insight into the progressive depletion of additives, build up of acidic products which lead to eventual degradation of the lubricant oil.

4.5.1.3 PCA Model of the Petrol Engine FTIR Spectra

The objective of this analysis was to investigate the FTIR spectra of these samples to monitor the progressive degradation of the lubricant oil. A PCA model was developed using the FTIR-ATR spectral data of the fresh oil (GTX) and 13 used oil samples collected from the petrol engine.

The raw data matrix was Pareto scaled without mean-centring (PARN). The two first PCs together describe 99.9% of the variation in the spectra data; PC 1 account for 99.7% while PC 2 explains 0.252% of the total variance.

The score plot of the data matrix is presented below. Each new variable point (t_1, t_2) corresponds to a FTIR spectrum of oil sample collected from the petrol engine.

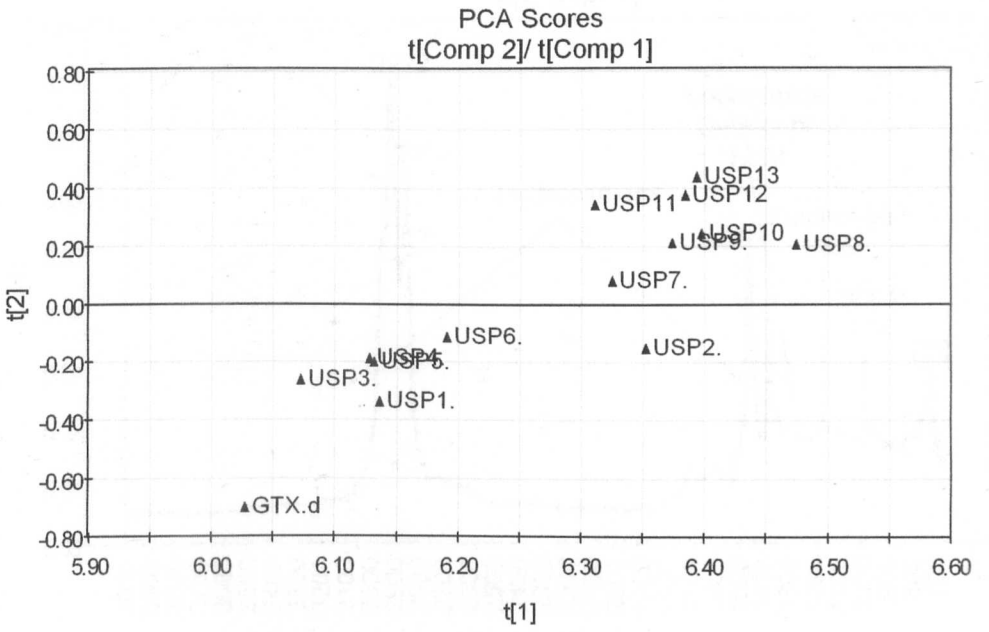


Figure 55: First two PC scores plot of petrol engine spectra data

The first two PC scores show that there are two distinct groups of oil samples. The observations labelled GTX to USP6 located on the left hand side of PC 1 and at the bottom of PC 2, while those labelled USP7 to USP13 are located on the right hand side of PC 1 and above the PC 2 axis. This corresponds to a separation of the first 2986 miles from the last 5119 miles of the total 8105 oil mileage. The third sample (USP2) is considered an outlier; it is not within the trend and appears unrelated to the other samples as it lies isolated from the groups in PC 1 and PC 2. To provide a cause-effect for the separation observed in this plot, we look at the corresponding loading plot for more information.

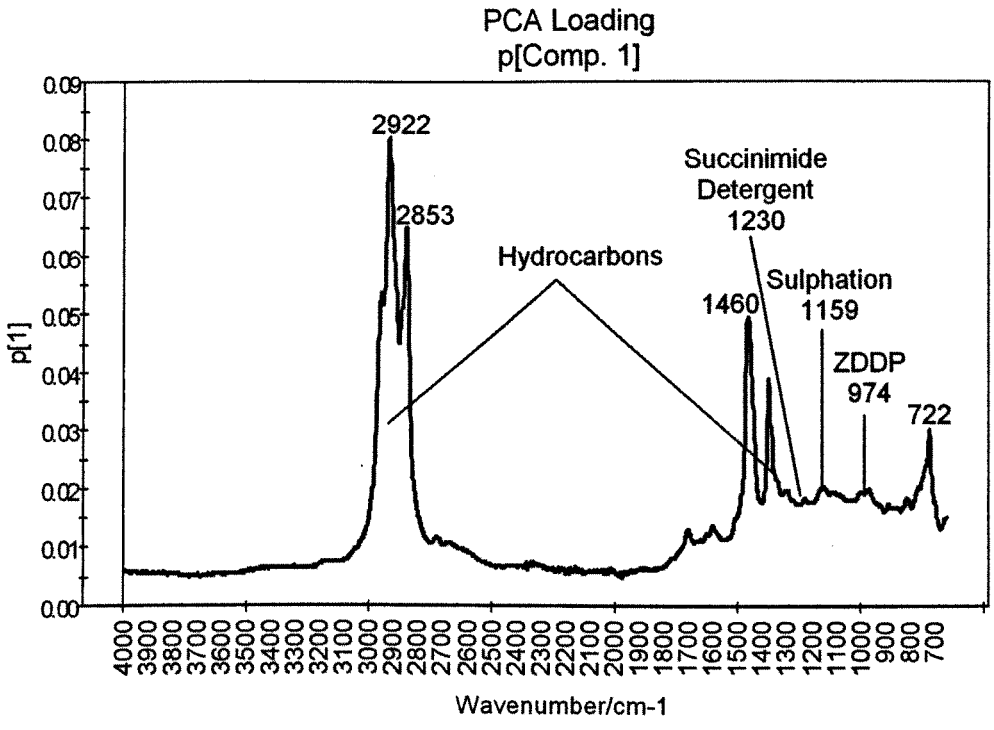


Figure 56: PC 1 loading plot of petrol engine spectra data

The p_1 loading plot summarises the most significant absorbance that corresponds to the separations of samples in the scores plot. The hydrocarbon peaks at 3000-2800 and 1500-1350 cm^{-1} appear to have the highest loadings. From 1800-700 cm^{-1}, a noticeable deviation from the base line is observed; this region can be associated with changes in the composition of the oils which occur during the service life of the oil. Due to the dominant hydrocarbon peaks in p_1 the other region is not fully explained therefore p_2 is examined for more details.

The positively and negatively correlated peaks in the p_2 loading plot below show the predominat changes occuring in the oil chemistry.

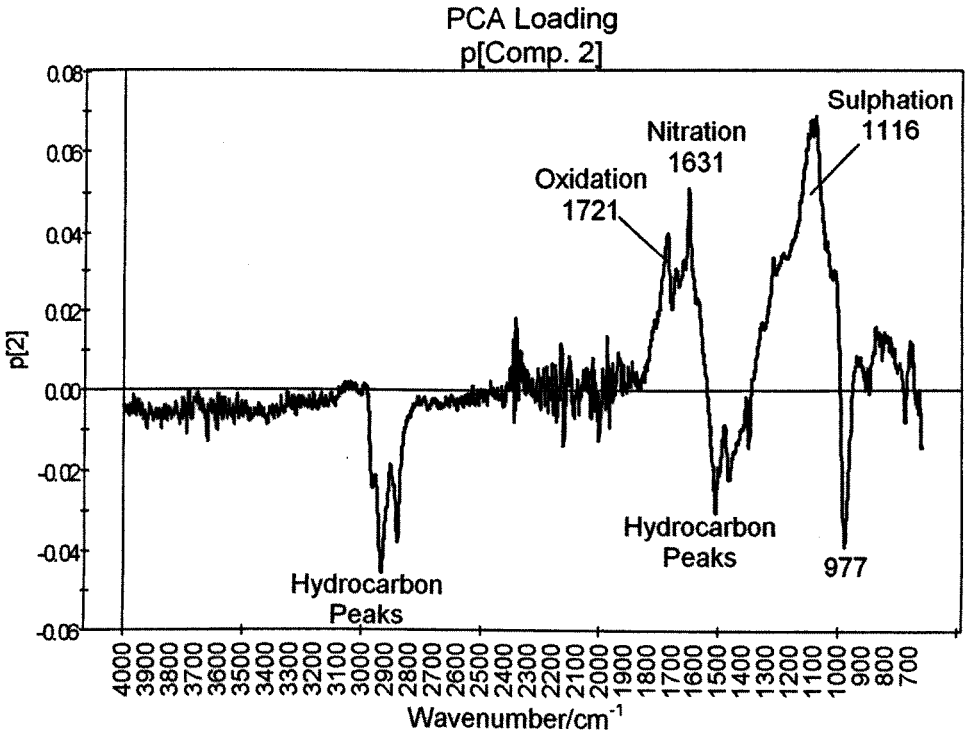


Figure 57: PC 2 loading plot of petrol engine data

It appears that the peaks at 1800-700 cm^{-1} dominate this plot. Positive peaks such as that observed at 1721 cm^{-1}, 1631 cm^{-1} and 1116 cm^{-1} have the highest loadings on p_2, this suggest that these peaks were sequentially formed during the service use of the lubricating oil. The negative peaks are the usual hydrocarbon peaks however a distinct peak at 977 cm^{-1} is also observed. These negative peaks imply that functional groups relating to these peaks are utilized during the progression of this oil.

Summarising the interpretation from the two plots the following possible conclusions are drawn:

- The separation between the first 2986 miles and last 5119 is a cause-effect of the changes occurring in the 1800-650 cm^{-1} region of the FTIR spectrum. It appears that at the latter mileage use of the oil there are increased degradation product characterised by peaks at 1721, 1631, and 1116 cm^{-1} respectively;
- The reduction of peak at 977 cm^{-1} is related to additive depletion in the oil;

- The results from PC2 suggest that by the end of the service life of this oil the chemical structures of the oil components are altered significantly due to rigorous conditions in the engine.

The contribution plot below shows the difference between the new oil at the start of this process and the condition of the oil after it has completed its year in service.

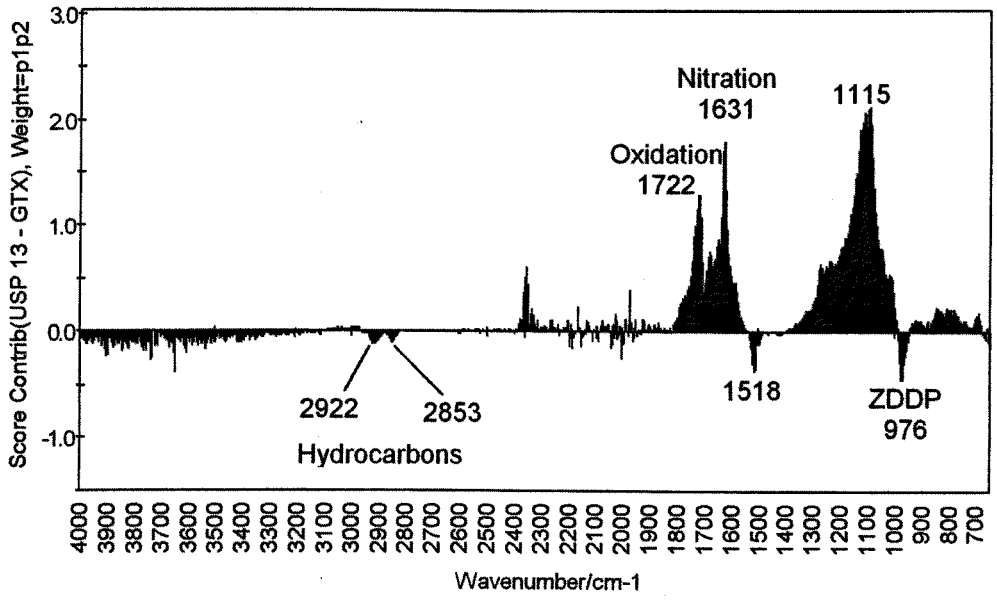


Figure 58: PCA contribution plot of difference between the fresh oil and the last oil (USP 13) sampled from the petrol engine

From this plot it is clearly evident that the chemical structure of this oil has been significantly altered. This conclusion is drawn from the hydrocarbon peaks that usually have higher absorbance and loadings are negative in this plot along with the additive peaks.

4.5.2 Peugeot 1.9 Diesel engine

4.5.2.1 Base Number Results and Trend Analysis

The base number of each sample was determined using the three methods of endpoint estimation. For each sample the titration was carried out three times, and the average base number for each method of calculation was recorded as shown in the table below.

Table 9: Base Number Results for Diesel Engine Oil Samples

Sample	Dates	Car Mileage	Oil Mileage	BN 1	BN 2	BN 3
GTD	01/07/2005	146974	0	10.2	9.8	10.3
USD 1	18/07/2005	149070	2096	9.4	9.1	9.6
USD 2	11/08/2005	150762	3788	9.0	8.7	9.0
USD 3	28/08/2005	152503	5529	8.6	8.4	8.8
USD 4	14/09/2005	154233	7259	7.9	7.9	8.2
USD 5	21/09/2005	155101	8127	8.1	8.0	8.2
USD 6	27/09/2005	155616	8642	7.4	7.2	7.6
USD 7	30/10/2005	157155	10181	7.0	7.0	7.2
USD 8	04/12/2005	159021	12047	6.3	6.2	6.5
USD 9	29/12/2005	160674	13700	6.7	6.7	6.8
USD 10	29/01/2006	162537	15563	6.6	6.4	6.7
USD 11	20/02/2006	163679	16705	5.8	5.8	5.8
USD 12	17/03/2006	165588	18614	7.8	7.4	7.7
USD 13	02/04/2006	166981	20007	6.6	6.5	6.8
USD 14	12/05/2006	170334	23360	6.7	6.6	6.7
USD 15	31/05/2006	172049	25075	6.4	6.1	6.4
USD 16	26/06/2006	174736	27762	5.9	5.7	5.9
USD 17	17/07/2006	177161	30187	6.3	6.1	6.3

The table gives the average base number results for each sample calculated by the different methods of endpoint estimation. The dates and mileages indicate the operating period of the lubricating oil. The base number trend for this sample is shown in the graph below.

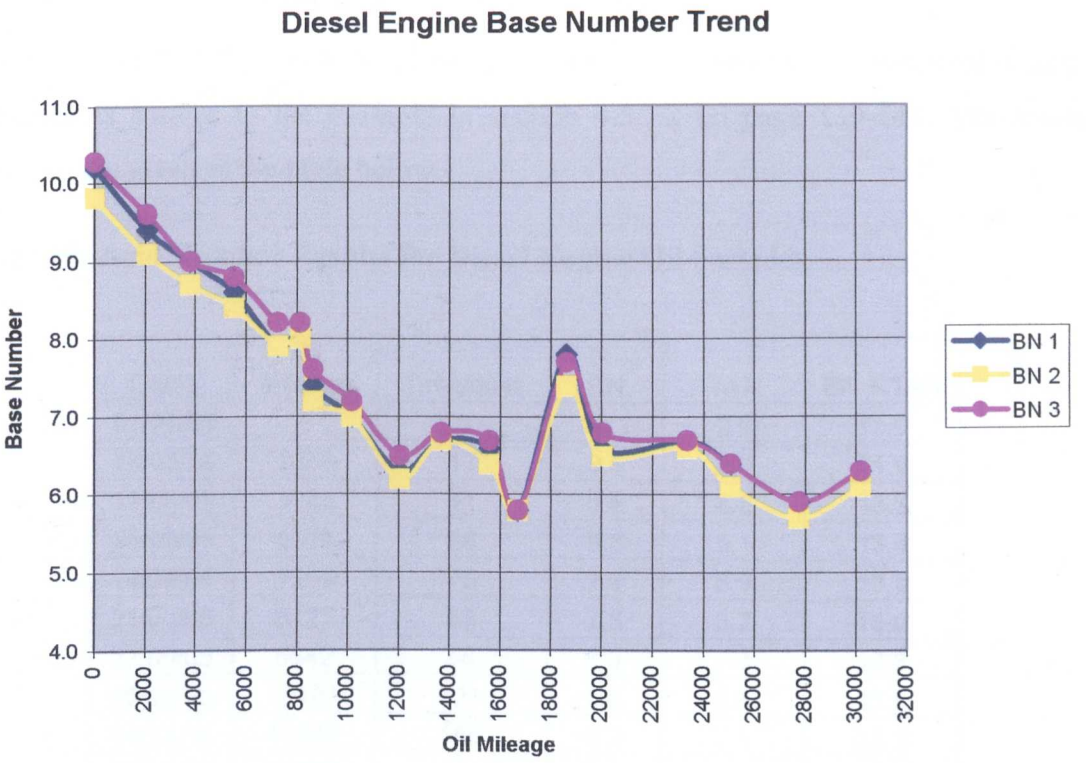


Figure 59: Base number against oil mileage plot for diesel engine

The plot of the three methods used to calculate base number appears slightly different however they are almost identical at some points. The general downward trend suggests that base number decreases as oil mileage increases. The observable fluctuation in base number value between 12000-20000 miles is associated with adding fresh oil into the engine (top-up). The results indicate that the alkaline reserve of the oil is replenished and thus the life of the lubricant is extended. As a result the base number of the oil at the end of its service life (6.3 mg KOH/g) is moderately good.

4.5.2.2 Acid Number Results and Trend Analysis

The total acid number for these oil samples were determined using linear least-squares calculations similar to the example in section 4.5.1.2 on page 139-141. The results obtained are given in the table below.

Table 10: Acid Number Results for Diesel Engine Oil Samples

Dates	Oil Mileage	Time/days	BN	TAN	BN + TAN
01/07/05	0	0	10.1	2.9	13.0
18/07/05	2096	17	9.1	2.8	11.9
11/08/05	3788	41	8.6	4.6	13.2
28/08/05	5529	58	8.3	5.1	13.4
14/09/05	7259	75	7.9	5.3	13.2
21/09/05	8127	82	7.3	5.7	13.0
27/09/05	8642	88	6.9	5.8	12.6
30/10/05	10181	121	6.8	6.6	13.5
04/12/05	12047	156	6.2	7.0	13.2
29/12/05	13700	181	6.7	5.0	11.7
29/01/06	15563	212	6.0	6.3	12.3
20/02/06	16705	234	5.6	7.9	13.5
17/03/06	18614	259	7.4	4.8	12.2
02/04/06	20007	275	6.5	6.2	12.7
12/05/06	23360	315	6.1	6.4	12.6
31/05/06	25075	334	5.8	7.2	13.0

The acid number trend for this oil samples is shown in the plot of acid number against oil mileage below.

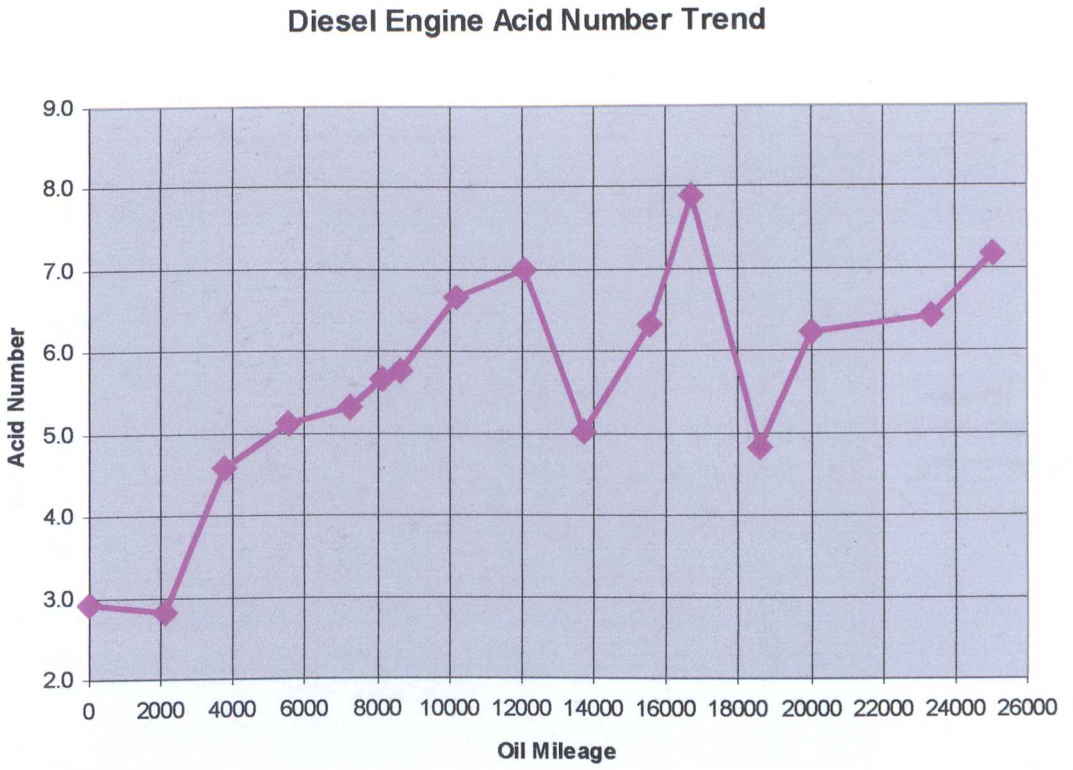


Figure 60: Acid number against oil mileage plot for diesel engine

A slight drop in acid number is observed between the new oil and the first used oil. The general trend shows that acid number increases with frequent use of the vehicle. The noticeable rise and fall between 12000 and 20000 miles is related to top-up of the engine oil with fresh lubricant, due to the large distance covered by this vehicle. It was necessary to add 350 mL at 12000 miles and 550 mL after 18000 miles. By the end of the test another 650 mL would have been required to restore the original level. The oil consumption of 52 mL/1000 miles (or 32 mL/Mm) is quite low considering the total distance covered. The addition of new oil promptly reduces the acid number, this is because the alkaline reserve additive in the new oil, effectively neutralises the acidic component of the used oil.

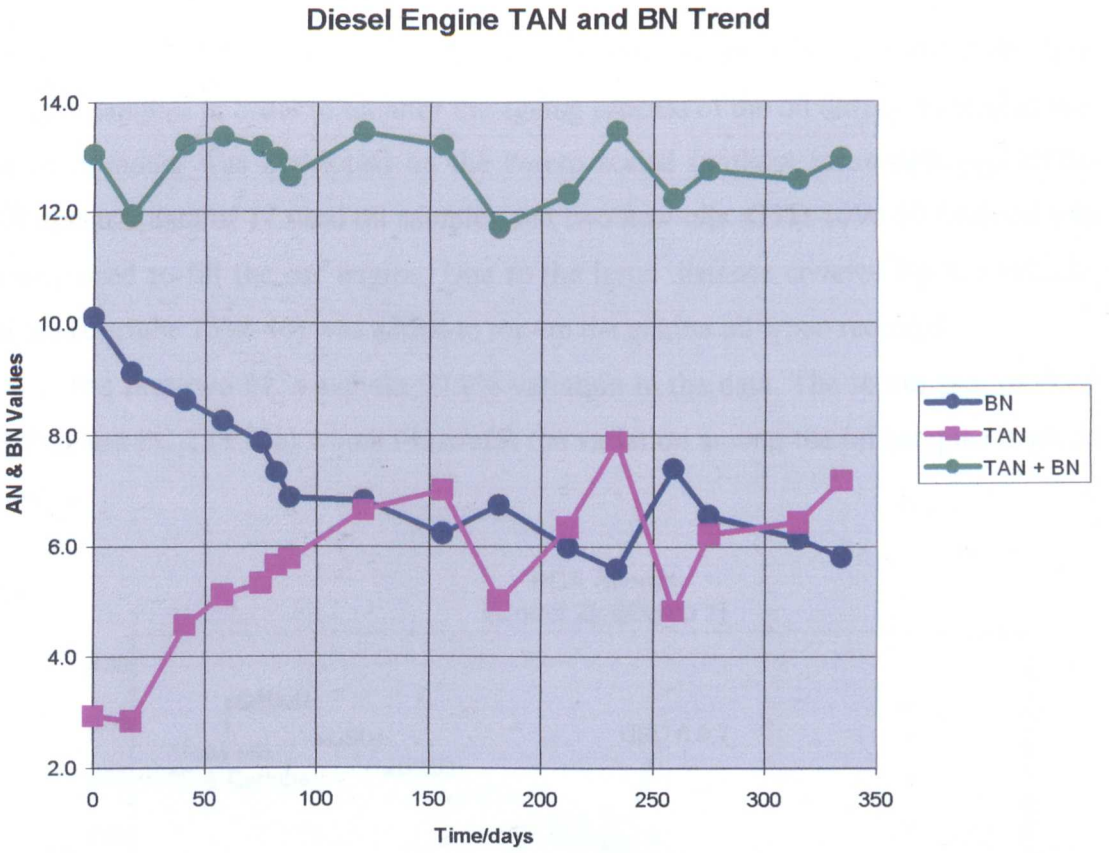


Figure 61: Acid and base number trend for diesel engine

The remarkable pattern exhibited by this engine oil sample is a direct effect of topping up the engine oil, resulting from frequent use of this vehicle. The first intersection of the two curves is observed after 100 days. Prior to the intersection the rate at which the base number curve declines is almost equivalent to the rise in acid number, this signifies acid neutralisation. It is believed that the base is consumed as acidity develops. Following the intersection a rise in acid number corresponds to a drop in base number. After the final top-up with fresh oil, the BN shows a progressive descrease and the TAN increases monotonically. This implies that sufficient alkali reserve remains in the oil.

For this series of samples the graph of TAN + BN against time gives, within experimental error, a constant value. This is due to the opposite trends observed in the separate measurements.

4.5.2.3 PCA Model of the Diesel Engine FTIR Spectra

The aim of this technique was to collectively explore the infrared spectra of these lubricant samples in order to monitor the ageing process of the oil during its service use. The PCA model was developed on the Pareto scaled (without mean-centring) FTIR-ATR spectral data of 17 used oil samples and two new oils. GTD 10W-40 fresh oil was initially used to fill the car engine. Due to the large distance covered by this vehicle, new oil (Carlube 15W-40) was added to top-up the engine oil when required.

The first two PC's explain 99.9% variation in the data. The scores plot of PC 1 (98.5%) and PC 2 (1.4%) which illustrates the variation among the oil samples is given below.

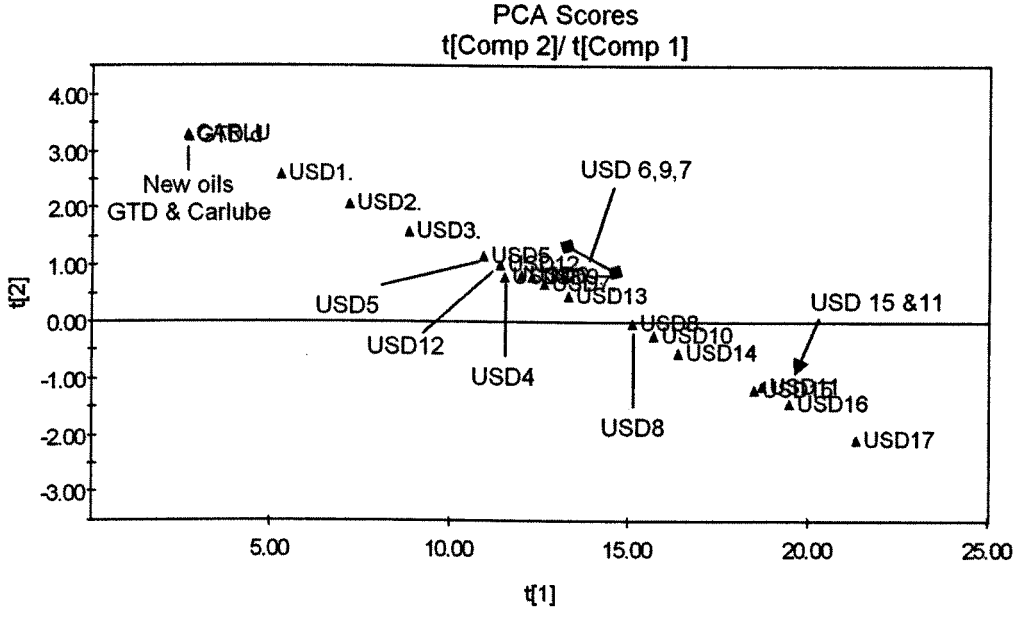


Figure 62: First two PC scores of diesel engine spectra data

The plot in general shows a downward trend, indicating continually changes in the chemical properties of the lubricant. The samples follow a descending order along the t_2 line (from new to old oil), and appear separated. There are two main groups; new to moderately used oil samples are located at the top while the aged oils are at the bottom. A few clusters are also observed which signify similarity among the samples. Given the knowledge about the operating cycle of the oil it is believed that the uneven changes

observed within the trend are effected by the addition of the fresh oil used to refill the engine.

The p1 plot below gives an overview of the FTIR spectrum of the new and used oil samples collected from the diesel engine.

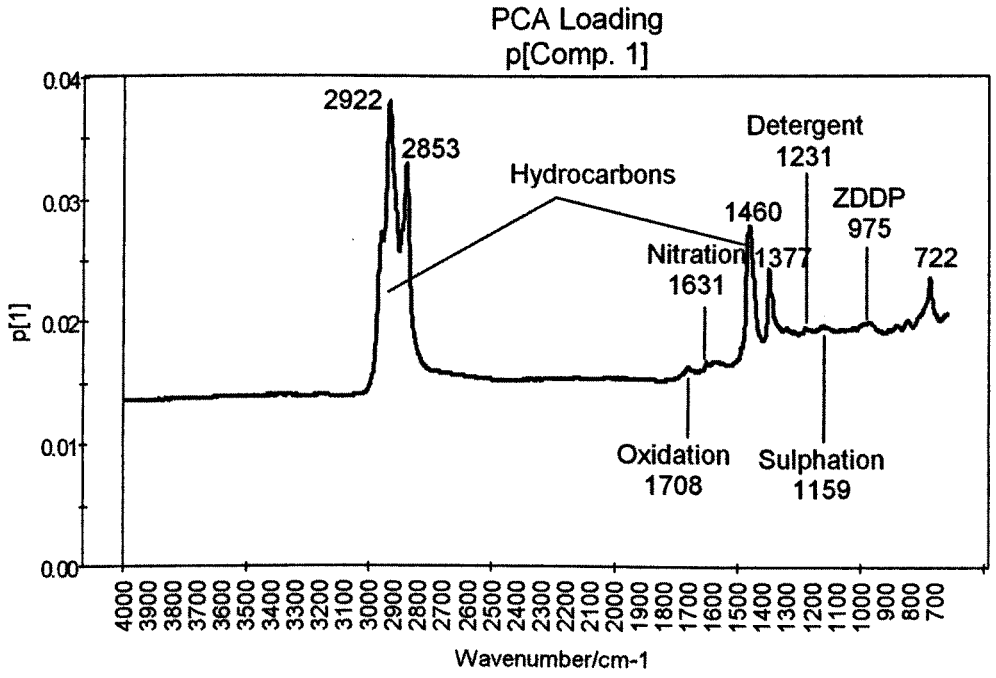


Figure 63: PC 1 loading plot of diesel engine spectra data

This plot effectively shows the unique characteristic of these diesel oil samples, a significant baseline shift. This elevation from the baseline corresponds to the ageing sequence of the oil; the consequential effect is the build-up of carbon particles which causes scattering of the infrared radiation. The labelled absorption peaks characterise the condition of the oil samples as degraded with some residual additives.

The p_2 loading plot which explain the remaining variation is shown below.

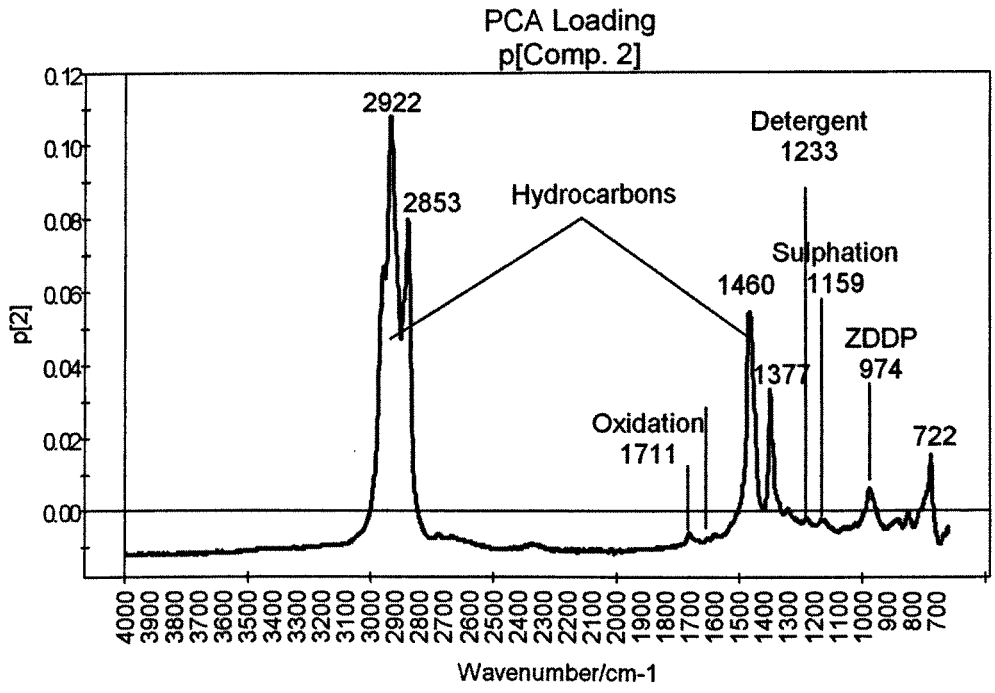


Figure 64: PC 2 loading plot of diesel engine spectra data

This plot describes the variation along the second principal component (t_2) in the scores plot, indicating the condition of the oil samples. Apart from the hydrocarbon peaks the only other positive peak is the absorption at 974 cm^{-1} which relates to the ZDDP additive. Therefore oil samples with positive weighting on t_2 still contain additive components. This suggests that the separation of samples along PC 2 is mainly due to the additive content of the oil sample.

The scores plot illustrates how the oil samples vary from each other, while the two loading plots explain the cause and effect of the variation observed. The absorption peaks in the two loading plots suggest that although the oil is contaminated (carbon particles) and degraded there is some remaining useful life in the lubricant sample after its cycle of operation exceeding 30000 miles.

From the PCA and the base number results it is evident that when top-up occurs the additive properties of the oil are replenished. This slows the development of degradation and prolongs the life of the lubricant.

4.5.3 Diesel engine sump samples from Castrol Road Test

4.5.3.1 Base Number Results and Trend Analysis

The base numbers for these samples was determined using the three curve fitting methods previously described. The average base number of three replicate titrations performed on each sample is given in the table below.

Table 11: Base Number Results for Diesel engine sump Test Oil Samples

Sample	BN 1	BN 2	BN 3
0 Hour	12.5	12.3	12.7
4 Hours	11.9	11.6	11.9
50 Hours	9.3	9.0	9.5
100 Hours	7.7	7.4	7.8
150 Hours	6.6	6.2	6.5
200 Hours	5.8	5.4	5.8
250 Hours	4.9	4.7	5.0
300 Hours	4.5	4.3	4.5
350 Hours	4.4	4.1	4.4
400 Hours	4.4	4.3	4.5

The base number trend for these oil samples is illustrated in Figure 65 below.

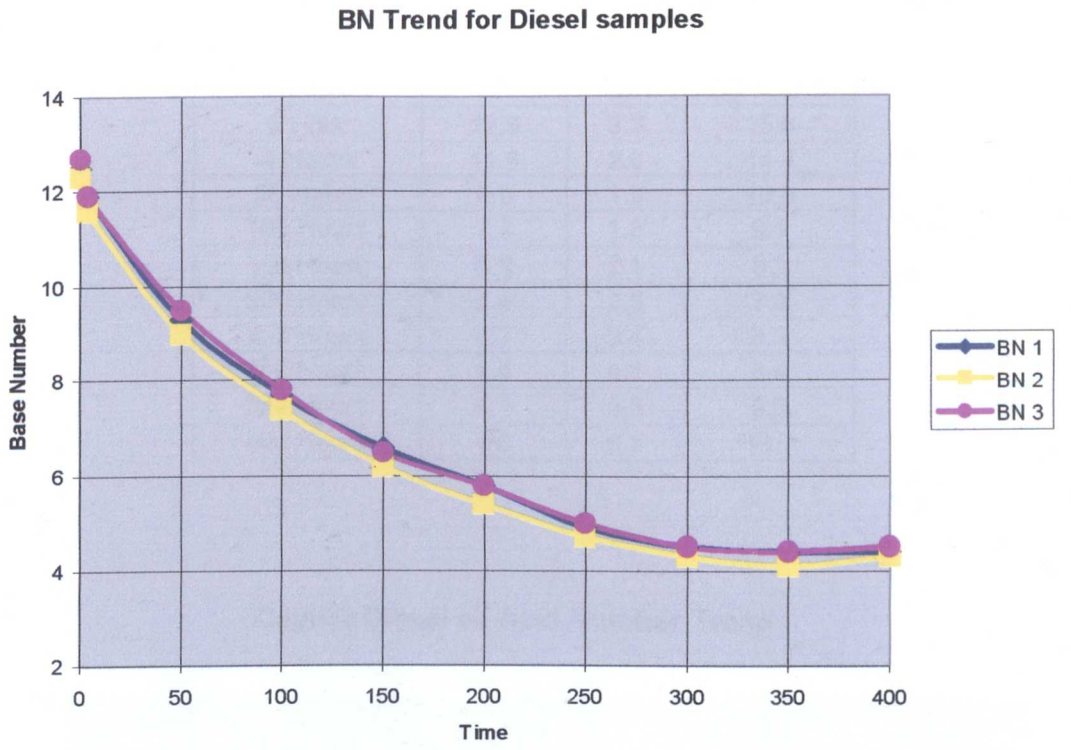


Figure 65: Base number against time plot for diesel engine sump test

The trend follows a decay curve that seems to reach a limiting minimum value. The base number of the oil samples decreases with increasing time interval. It appears that the oil degenerates considerably after 4 hours before reaching a constant at 300 hours. After 400 hours of operation the lubricant oil with initial base number of 12.7 mg KOH/g has depleted to 4.5 mg KOH/g, this decline in BN is indicative of the thermal and oxidative stability of the lubricant.

4.5.3.2 Acid Number Results and Trend Analysis

The total acid number for these oil samples was determined using the least-squares curve fit method and calculations similar to the example described in section 4.5.1.2. The results obtained are given in the table below.

Table 12: Acid Number Results for Diesel Engine Sump Test Oil Samples

Sample	BN	TAN	BN + TAN
0 Hour	12.3	3.3	15.6
4 Hours	11.6	2.8	14.4
50 Hours	9.0	1.9	10.9
100 Hours	7.4	1.8	9.1
150 Hours	6.2	2.1	8.2
200 Hours	5.4	2.5	7.9
250 Hours	4.7	3.4	8.1
300 Hours	4.4	4.1	8.4
350 Hours	4.1	5.5	9.6
400 Hours	4.0	6.7	10.7

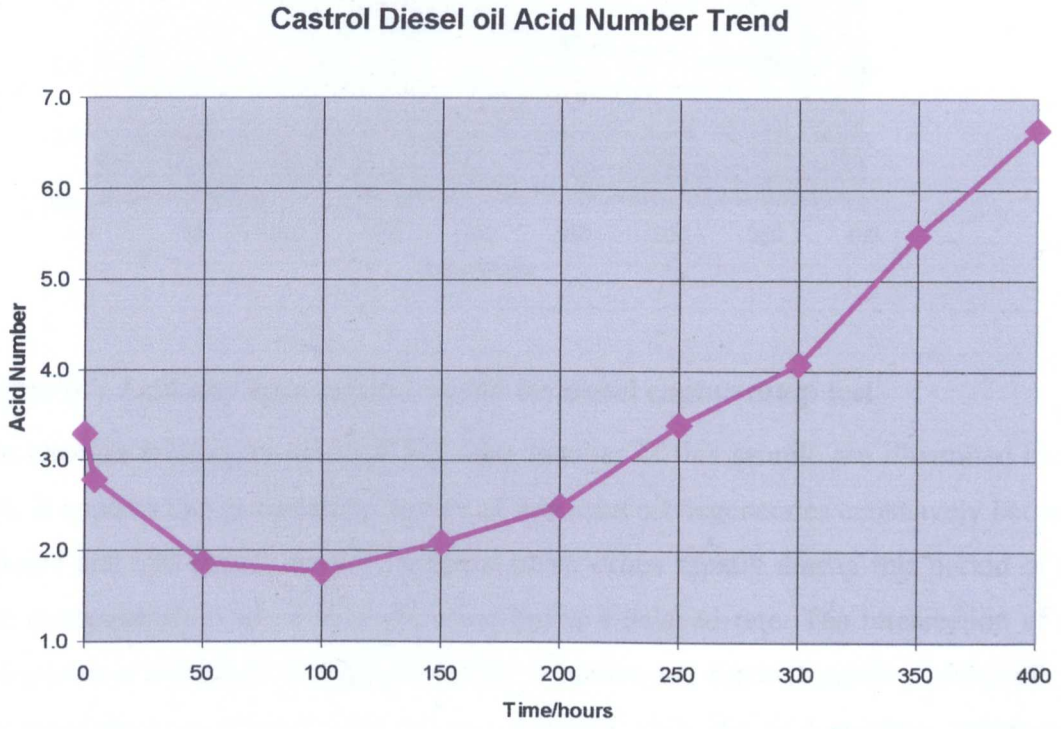


Figure 66: Acid number against time plot for diesel engine sump test

The acid number initially drops rapidly, from the fresh oil (0 hour) at 3.3 mg KOH/g to 2.8 mg KOH/g after 4 hours then 1.9 mg KOH/g after 50 hours test and slowly to 1.8 mg KOH/g after 100 hours. The first rise is observed after 100 hours and then a sustained growth in acid number as the test continues. After 400 hours the total acid

number of the lubricant oil is 6.7 mg KOH/g, this is relatively high considering the amount of alkaline reserve in the new oil (12.7 mg KOH/g).

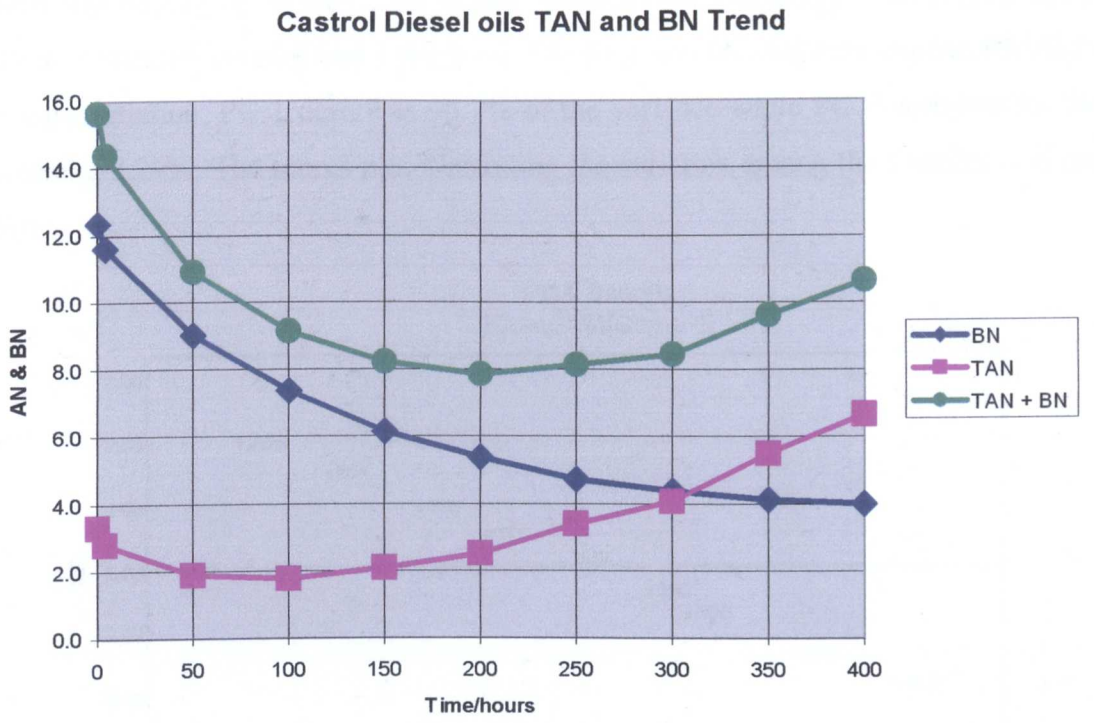


Figure 67: Acid and base number trend for diesel engine sump test

The changes relating to the acid and base number of this sample are illustrated in the plot. It appears that the alkaline content of lubricant oil degenerates extensively between 4 hours and 300 hours; the base number curve drops rapidly during this period of the test, consequently acid number increases but at a delayed rate. The intersection of the two curves at 300 hours is indicative of the oxidative and thermal stability of this oil. At this point the base number approaches a constant while the acid number continues to rise, this suggests that the build up of acidic species is more rapid than the rate of acid neutralisation by the base additive of the oil. However the development of acidity in the oil was delayed this is possibly the major function of the fresh oil therefore unable of completely neutralise acidity for the duration of the test.

The TAN + BN curve declines rapidly in the early stages. Later in the test the values become steady before a final increase near the end of the test.

4.5.3.3 PCA Model of the Diesel Engine Sump Test FTIR Spectra

The objective of this technique was to explore the infrared spectra of these lubricants in order to uncover effects occurring in time during service use of the lubricant oil. A PCA model was developed on the Pareto scaled (without mean-centring) FTIR-ATR spectral data of 9 used oil samples and 1 fresh oil. The first two PCs together explain 99.9% of the data variation; PC 1 describes 96.7% of the variance while PC 2 accounts for the remaining 3.29%. The scores plot illustrating the variation among the samples is given below.

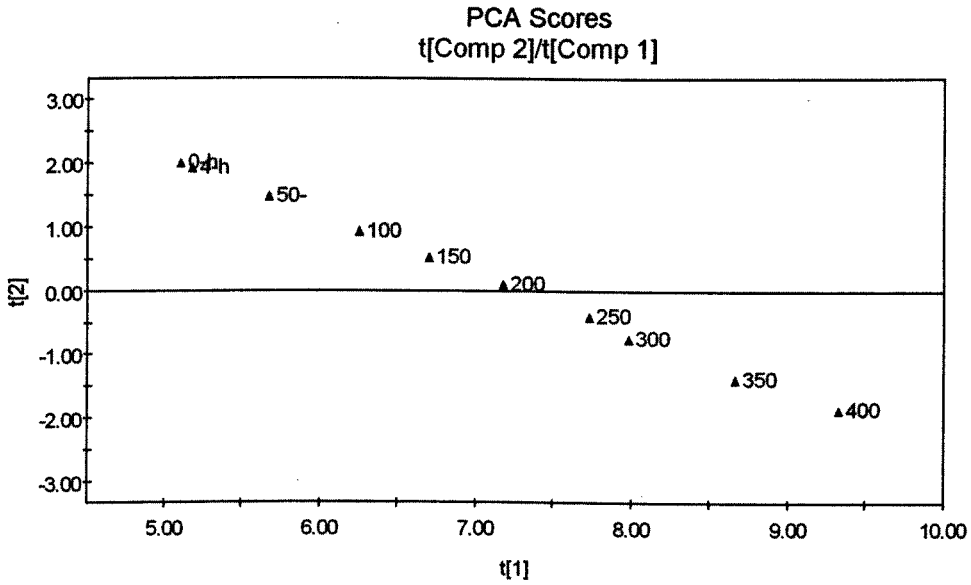
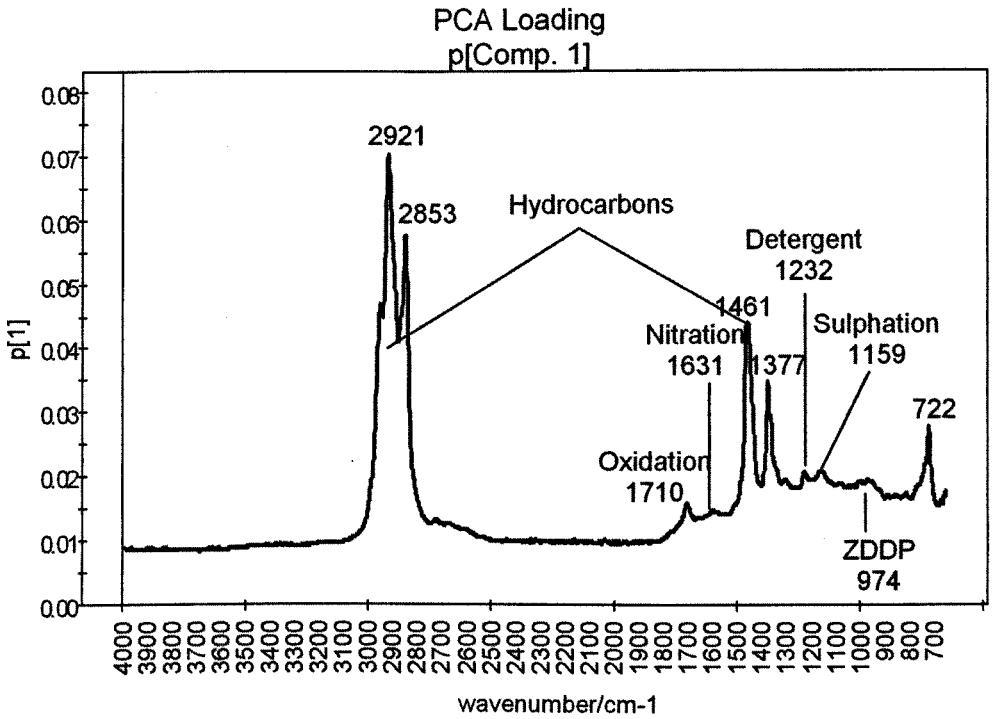


Figure 68: First two PC scores plot of diesel engine sump test spectra data

The pattern in the scores plot is outstandingly clear. The almost perfect linear descending trend indicates changes in the properties of these oils as a function of time. Evidently there is progressive ageing of this oil, the similarity between the fresh oil (0 hours) and oil sampled after 4 hours suggest that only slight change occurred, whilst the distance between the new oil and 400 hours oil sample signify extensive alteration in the properties of the lubricant oil.

The loading plots below give an overview of the FTIR spectrum of the oil samples that provide a cause effect for the pattern observed in the scores plot.



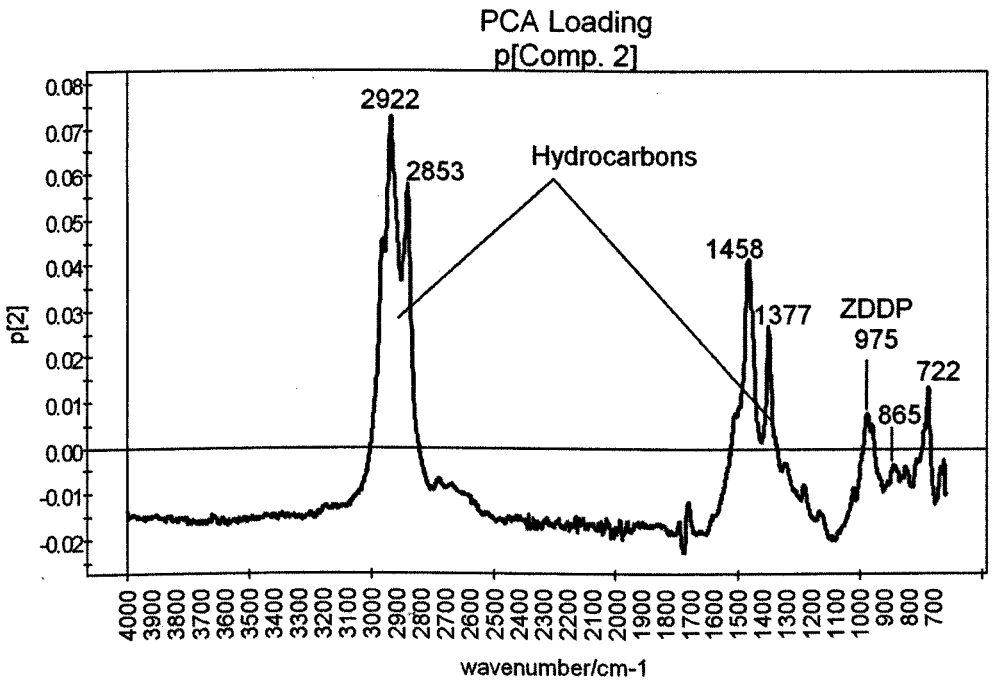


Figure 69: PC 1 and 2 loading plots of diesel engine sump tests

The significant shift in baseline in p_1 is indicative of the quantity of carbon particles present in this oil due to the extent of test duration, this is effect can be associated with oil samples below the t_2 line in the scores plot. Depreciation of these oil's properties are evidently revealed through peaks at 1710 cm^{-1}, 1631 cm^{-1} and 1159 cm^{-1} with diminishing peak at 975 cm^{-1}, which are typical chemical degradation parameters. The p_2 loading plot illustrates the changes occurring during the test. The additive peak uncovered at 975 cm^{-1} which ascends above the axis indicate the oil samples located on the upper part of the t_2 line in the scores plot contains this additive. This signifies that after 200 hours of the test the function of the additive is fatigued and is possibly eliminated by the end of the test at 400 hours. This may be a reason for the prominent acid number trend.

The results shown in this chapter have demonstrated the progress and innovation achieved in extraction and interpretation of objective information from the experimental data. The acid and base number graphs, PCA scores and loading plots have contributed significantly to understanding the progressive degradation of lubricating oils during service use.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Many detailed conclusions that have arisen directly from the results have been presented in Chapter 4. This chapter reports overall conclusions arising from the development of novel methods and enhancement by chemometric procedures of previously used techniques in studying engine lubricant degradation. These procedures for lubricant testing are numerous, expensive and labour intensive; however these assessments are an essential part of lubricant development. As a result, cost effective and rapid testing methods are desirable. The areas of improvement described and results obtained have confirmed that this study contributes considerably to the research in this field.

Top Ring Zone Sampling

Previous workers[22-26] have proved that this technique is an effective test method for studying engine oil degradation. However it does require considerable skill to obtain data and system breakdowns are not uncommon. The application of multivariate data analysis provided detailed and visual insights into degradation conditions of the various lubricant formulations tested. The differences between the performance levels of each formulation were established[65-67]. The comprehensive information obtained by this analysis is unachievable from a data table, even though the spectral data were converted into numerical values, which indicate degradation parameters. The results demonstrate the feasibility of the chemometric approach to top ring zone sampling, making the technique more informative and robust[66-67].

Acid and Base Number

The modification to the titration equipment has proved satisfactory. The novel nonlinear least-squares modelling and least-squares curve fit methods used for calculating base number were shown to be successful in meeting the target objective set in Chapter 2, section 2.4.3. The models were able to detect automatically very low and high levels of alkaline reserve in new and used oil samples. More than hundred and fifty lubricant samples leading to over five hundred titrations were performed without subjective intervention in the calculations. The integration of these models provides a statistically

accurate measure of base number. The calculation algorithms were automated; thereby removing operator bias; thus offering reliability and robustness to the conductimetric titration technique.

The conductimetric back-titration method previously established for acid number measurement was adopted for acid number determination of the time series sets of lubricant samples. The reproducible titration curve shape and progressive trends in the acid number values obtained demonstrate the capability of this method and verify the stability of the titration equipment. This study illustrates improved measurement reliability and repeatability of the titration technique compared with the current standard potentiometric acid number methods (ASTM D 664 or IP 177).

Intersecting lines are commonly encountered in a very wide range of scientific studies. In estimating the transition from one phase to another, the point of intersection between two lines is generally used to identify the abrupt change. The nonlinear least squares model developed here, would be appropriate to such types of experimental data, particularly when there is observable curvature between the linear regions.

FTIR Analysis

The FTIR/ATR instrument offered a quicker easy-to-operate and much more consistent alternative to the transmission technique. The quality of spectra obtained greatly facilitated interpretation. However for routine analysis, interpreting a large volume of spectroscopic data is lengthy and labour intensive. It would be challenging to analyse simultaneously several spectra and draw comprehensive conclusions. Prior to this work, methods such as "Spectral Subtraction" suggested by J.P Coates and L.C Setti[30-31] and "Simple Trending" proposed by J. R. Powell and A. M. Toms[34] were used for identifying degradation parameters. These were time consuming, required skilled and experienced operators and were subject to human bias.

The utility of chemometric techniques are more consistent when compared to other methods, subjective judgement of how to perform the subtraction and the choice of reference are eliminated[68].

The principal component model that was used to summarise the FTIR spectra of all the lubricant oil samples used Pareto scaling. This provided a PCA model which simplified interpretation and understanding of the relationships between and properties of the engine oil samples.

The PCA model recognized the deviation among the formulated new lubricants, these relationships were illustrated in the scores and loading plots. The results obtained were in agreement with the base number results.
PCA developed on the low base number lubricant samples spectral data demonstrated that the decline in the alkaline reserve are highly related to build up of combustion products, water contamination and exhaustion of the additive packages due to prolonged used of the lubricating oil.

The PCA model proved valuable for studying concurrently the FTIR spectra of the time series set of lubricants. The PCA scores plots highlighted the changes occurring while the loading plots offered visual outline of how additives deplete with evolution of degradation species. A PCA model contribution plot on the of the petrol engine oil samples indicated the condition of the lubricant oil after a year of operational condition.

It is practically impossible to inspect collectively and extract significant and subtle effects from the raw spectra. This application illustrates the power of PCA in detecting outliers, reducing the size of the data whilst optimising interpretation and managing the large volume of data obtained in this work.

This work has shown the concept of chemometric applications for monitoring changes in chemical properties of lubricants during operative conditions. Detailed understanding of how and when lubricants degrade will ultimately lead to optimization of lubricant formulations. These procedures are rapid, economical and accurately detect general degradation parameters. It is therefore feasible for condition monitoring of lubricant performance to be based on IR measurement. In some cases it may be possible to do this work on the vehicle or in the company maintenance facility without the need to send samples to a laboratory. The prospect of this can benefit such diverse fields as offshore

testing, military vehicles, railway locomotives, cargo vessels and tankers without withdrawing them from service.

5.2 Recommendations for Further Work

Since the reliability of the titration equipment and the computer programme has established, it is suggested that further acid number titration measurements be performed. This study should include the investigation of acid content in fresh oils and development of a nonlinear model to determine the titration endpoint.

Periodic sampling of used oil from vehicles can be time consuming, as an alternative real-time FTIR monitoring is suggested. This procedure may be performed on a short period engine test, with the application of PCA rapid indication of the reaction sequence and chemical changes occurring will be identified. In the case of an elaborate test, the process can be immediately shutdown at the sign of any problem.

The database should be expanded to include other frequent tests such as engine wear and viscosity measurement. The utilisation of chemometric techniques to explore such datasets would enhance information extraction, and may reduce testing procedures by showing correlation between test methods.

In general, a statistical approach to designing experiments and process monitoring is recommended, this would provide efficient experimental procedures and consequently save time and reduce cost.

References

1. Hillier, V.A.W. Fundamentals of motor vehicle technology. 4th ed. 1995, Chlenham: Stanley Thornes Ltd.
2. Tung, S.C. and M.L. McMillan. Automotive tribology overview of current advances and challenges for the future. Tribology International, 2004. 37(7): p. 517-536.
3. Heisler, H. Vehicle and engine technology. 2nd ed. 1999, London: Arnold; p. 294-305.
4. Andersson, B.S. Company perspectives in vehicle tribology- Volvo. In: 17th Leeds-Lyon Symposium on Tribology-Vehicle Tribology. 1991. Oxford UK: Elsevier Ltd.
5. McCabe, M., Alison F. Overview of EU oil quality and emissions legislation developments[Online]. [cited 2006 March 17]; Available from: URL: http://www.osd.org.tr/15.pdf
6. Bell, J.C. Gasoline engine valve train design evolution and the antiwear requirements. Proceedings of the I MECH E Part J Journal of Engineering Tribology, 1998. 212(4): p. 243-257.
7. Moller, U.J., Boor,U. Lubricants in operation, ed. A.R. Lansdown. 1996, Suffolk: Mechanical Engineering Publications Limited.
8. Infineum International Limited. API engine oil classification [Online].2004 [cited 2005 Aug 24]; Available from: URL: http://www.infineum.com/information/api-viscosity-2004.html
9. American Petroleum Institute. Engine oil licensing and certification system (EOLCS). [Online] [cited 2005 Aug 24]; Available from: URL:http://www.api.org/certifications/engineoil.html
10. Prince, R.J. Base oils from petroleum. In: Chemistry and technology of lubricants, Mortier R.M., Orszulik, S.T. editors. 1997, Blackie Academic and Professional: London. p. 1-33.

11. Federal Trade Commision. Divestiture required to maintain competition and prevent increased prices in U.S. and Canadian market for group II paraffinic base oils. [Online] 2002 Sep 27 [cited 2005 Aug 24]; Available from: URL:http://www.ftc.gov/opa/2002/09/shellpennzoil.htm
12. Kramer, D. C., Lok, B. K., Krug, R. R., Rosenbaum, J.M. Chevron Texaco Global Lubricants 2003. The advent of modern hydroprocessing - The evolution of base oil technology machinery lubrication magazine.
13. Bui, K., "Synthetics II," Lubricants world, November 1999.
14. Singh, H. Lubricants Technology - An Overview. In: Science in Africa Online Science Magazine [Online]. 2002 [cited 2005 Aug 15] Available from: URL: http://www.scienceinafrica.co.za/2002/november/lubes.htm
15. Davis, F.A. and T.S. Eyre, The effect of a friction modifier on piston ring and cylinder bore friction and wear. Tribology International, 1990. 23(3): p. 163-171.
16. Colyer, C.C., and Gergel, W.C., Detergent and Dispersant. In: Chemistry and technology of lubricants, Mortier, R.M., Orszulik, S.T., editors. 1997, Blackie Academic and Professional: London. p. 75-95.
17. Lazar, A. and Carter, J.C. (1946) US Patent 2,402,288.
18. Kenneth, R.B., Diesel engine service. 1984, Reston, Virginia: Reston Publishing Company.
19. Rasbergr, M., Oxidation degradation and stabilisation of mineral oil base lubricants. In: Chemistry and technology of lubricants, Mortier R.M., Orszulik, S.T., editors. 1997, Blackie Academic and Professional: London. p. 96-143.
20. Robinson, N., Monitoring oil degradation with infrared spectroscopy. In: Wear Check Technical Bulletin. 1998.
21. Coy, R.C., Practical applications of lubrication models in engines. Tribology International, 1998. 31(10): p. 563-571.
22. Bush, G. P., Fox, M. F., Picken, D. J., Butcher, L. F. Composition of lubricating oil in the upper ring zone of an internal combustion engine. Tribology International, 1991. 24(4): p. 231-233.
23. Cupples, S.D. Lubricant condition in the upper piston ring zone of single cylinder diesel Engines under operating conditions. PhD [thesis]. Leicester: DeMontfort University; 1992.

24. Thomson, A.L. An accelerated method to assess lubricant degradation in the piston ring zone of spark ignition engines. PhD [thesis]. Leicester: De Montfort University; 1995.
25. Pease, N. Top ring zone oil sampling in gasoline engines. PhD [thesis]. Leicester: De Montfort University; 2001.
26. Datoo, A.N.G. Kinetic comparison of oil degradation using the Petter W-1. PhD [thesis]. Leicester: De Montfort University; 2003.
27. Oxidation and Bearing Corrosion Engine Test IP 176 Petter W-1.
28. Pavia, D. L., Lampman, G.M., Kriz, G.S. Introduction to spectroscopy. 3rd ed. 2001, London; Fort Worth, Tex.: Harcourt College Publishers.
29. Cooley, J.W., Tukey, J. W. An algorithm for the machine calculation of complex Fourier series. Mathematics of Computation, 1965. 19: p. 297-301.
30. Coates, J.P., Setti, L. C. Infrared Spectroscopy as a tool for monitoring oil degradation. ASTM STP916 Philadelphia, 1981: p. 57-78.
31. Coates, J.P. Infrared Spectroscopy methods for the study of lubricant oxidation products. ASLE Transactions, 1985. 29(3): p. 394-401.
32. Zieba, J. Examination of lubricating oils by infrared spectroscopy. Forensic Science International, 1985. 27(1): p. 31-39.
33. Geach, A. Infrared analysis as a tool for assessing degradation in used engine oil. In: Wear Check Technical Bulletin. 1993.
34. Toms, A.M., Powell, J. R. Molecular analysis of lubricants by FTIR spectrometry. In: P/PM Technology. 1997. p. 58-64.
35. Rubinson, K.A., Rubindon, J. F. Contemporary instrumental analysis. 1st ed. 2000, New Jersey: Prentice-Hall. 318.
36. Armitage, D.A., Fakir, A.H., Fox, M., Jerrison, P., Smith, D., Wheeler, S. Automation of total base number determination of new and used lubricating oils. In JOAP International Condition Monitoring. 1989. Mobile, Alabama.
37. Determination of base number of petroleum products- Conductimetric titration method IP400/94.
38. Determination of acid- Potentiometric titration method IP177/96.
39. Pickering, S.M. Automation of acid and base number determinations of new and used lubricating oils. PhD [thesis]. Leicester: De Montfort University; 1993.

40. UMETRICS, SIMCA-P 10.5. 2004, UMETRICS AB: Sweden.
41. MINITAB, Inc., MINITAB STATISTICAL SOFTWARE. 2000, MINTAB, Inc: United State.
42. The MathWorks, MATLAB 7. 2004, The Math Works, Inc: Natick.
43. Microsoft Windows XP. Microsoft Excel. 2002, Microsoft Corporation: United Kingdom.
44. Wise, B.M., Gallagher, N B., Bro, R., Shaver, J M., Windig, W., Koch, R S. PLS_Toolbox. 2004, Eigenvector Research, Inc: Manson.
45. Wold, S. Chemometrics; what do we mean with it, and what do we want from it? Chemometrics and Intelligent Laboratory Systems, 1995. 30(1): p. 109-115.
46. Massart, D.L., Vandeginste, B.G.M., Buydens, L.M.C., De Jong, S., Lewi, P.J., Smeyers-Verbeke, J. Data handling in science and technology. In: Handbook of Chemometrics and Qualimetrics, Rutan, S., Walczak, B. editors. 1997. p. 1.
47. Cooper, J.B. Chemometric analysis of Raman spectroscopic data for process control applications. Chemometrics and Intelligent Laboratory Systems, 1999. 46(2): p. 231-247.
48. Martens, H., Naes, T. Multivariate calibration. 1989, Chichester: John Wiley &son.
49. Miller, J.N., Miller, J.C. Statistics and chemometrics for analytical chemistry. 4th ed. 2000, Harlow: Prentice Hall. 57-64.
50. Eriksson, L., Johansson, E., Kettaneh-Wold, N., Wold, S. Multi-and Megavariate data analysis principles and applications. 2001, Sweden: Umetric AB.
51. Wold, S., Esbensen, K., Geladi, P. Principal component analysis. Chemometrics and Intelligent Laboratory Systems, 1987. 2(1-3): p. 37-52.
52. Chatfield, C., Collins, A.J. Introduction to multivariate analysis. 1995, Cambridge: Chapman &Hall.
53. Pearson, K. On lines and planes of closest fit to systems of points in space. In: Philosophical Magazine. 1901. p. 559-572.
54. Malinowski, F., Howery, D. Factor analysis in chemistry. 1980, New York: Wiley.

55. Ramos, L.S., Beebe, K.R., Carey, W.P., Sanchez, E., Erickson, B.C, Wilson, B.E., Wangen, L.E., Kowalski, B. R. Chemometrics. Analytical Chemistry, 1986. 58: p. 249R-315R.
56. Joliffe, I.T. Principal Component Analysis. 1986, New York: Springer-Verlag.
57. Strang, G. Linear algebra and its applications. 1988, USA: Harcourt Brace Jovanovich.
58. Golub, G.H., VanLoan, C. F. Matrix computations. 3rd ed. 1996, Baltimore and London: The Johns Hopkins University Press.
59. Wold, H. Nonlinear estimation by iterative least squares procedures. In: Research papers in statistics. David, F. editor. 1966, Wiley: New York. p. 411-444.
60. Brereton, R.G. Chemometrics: Data analysis for the laboratory and chemical plant. 2003, Chichester: Wiley.
61. Kowalski, B., Gerlach, R., and Wold, H. Chemical systems under indirect observations, In: Systems under indirect observations, Joreskog, K., Wold, H. editors. 1982, North-Holland: Amsterdam. p. 191-209.
62. Agnar, H. PLS regression methods. Journal of Chemometrics, 1988. 2(3): p. 211-228.
63. Wold, S., Albano, C., Dunn III, W. J., Edlund., Esbensen, K., Geladi, P., Hellberg, S., Johansson, E., Lindberg , W., and Sjöström, M. Multivariate data analysis in chemistry. In: Chemometrics, mathematics and statistics in chemistry, B.R. Kowalski, editor. 1984, Reidel: Dordrecht. p. 17.
64. Miller, J.N., and Miller, J. C. Statistics and chemometrics for analytical chemistry. 4th ed. 2000, Harlow: Prentice Hall. p. 135- 136.
65. Aruna, M.A., Fox M.F. Correlation of field, laboratory and standard lubricant tests using multivariate analysis. Proceedings of the I MECH E Part D Journal of Automobile Engineering, 2004. 218(2): p. 195-201.
66. Aruna, M.A., Fox M.F, Differentiation of lubricant degradation in the piston ring groove and crown land by multivariate data analysis. Proceedings of the I MECH E Part D Journal of Automobile Engineering, 2004. 218(12): p. 1503-1511.

67. Aruna, M.A., Datoo, A., Fox M.F, Differentiation between 'good', 'borderline', and 'poor' ASTM lubricant standards by ring zone sampling and multivariate data analysis. Proceedings of the I MECH E Part D Journal of Automobile Engineering, 2006. 220(2): p. 177-185.

68. Aruna, M.A., Fox M.F. FTIR Spectroscopy and Multivariate data Analysis Approach for Differentiating between 'Good', 'Borderline', and 'Poor' ASTM Lubricant Standards by Ring Zone Sampling. In: The Gordon Conference on Statistics in Chemistry and Chemical Engineering. 2005. Boston USA.

Appendix A

```
10 REM ***Oil analysis master program***
20 KEY OFF:SCREEN 0:COLOR 7,1:CLS:BANDS=63:OUT 772,BANDS:T=TIMER
25 DEF SEG=0:POKE 1047,PEEK(1047) OR 64:POKE 1048,PEEK(1048) OR 64:DEF
SEG
30 LOCATE 10,20:PRINT "Press any key to run the set-up routine."
35 V$="+03846":DVM=64000!:FRED=64128!:PRNSTAT=64256!:CHECKSUM=0
40 DATA
85,137,229,139,94,6,138,15,139,95,1,186,4,3,181,0,250,180,43,236,12,0,
120,2,180,45,136,39,73,180,64,67,236,136,7,36,112,56,224,117,247,236,5
8,7,117,243,36,15,12,48,136,7,128,236,16,226,230,128,103,252,49,251,93
,202,2,0
45 DATA
85,137,229,139,126,10,139,21,180,54,205,33,61,255,255,116,18,247,227,2
47,225,139,126,8,137,21,139,126,6,137,5,93,202,6,0,186,255,255,235,237
50 DATA
85,137,229,139,94,6,186,0,0,184,0,2,205,23,134,224,137,7,93,202,2,0
55 FOR X=0 TO 65:READ Y:CHECKSUM=CHECKSUM+Y:POKE DVM+X,Y:NEXT X
60 FOR X=0 TO 39:READ Y:POKE FRED+X,Y:NEXT X
65 FOR X=0 TO 21:READ Y:POKE PRNSTAT+X,Y:NEXT X
70 DIM
A$(7),B$(2),X%(28),Y(10),D(3,10),R(10),A(5),X(5,5),W(5),E(5),V(3),V0(3
),C(3),B(3),S(3),Z(3),Z0(3),G(1,3):FOR I=1 TO 3:B(I)=20:NEXT I
75 IF CHECKSUM<>7081 THEN CLS:LOCATE 10,18:PRINT "Machine Code Data
Error - Programme Invalid":LOCATE 1,1:NEW:END
80 IF INKEY$<>"" THEN 100
85 IF (TIMER-T)<3 THEN 80
90 CLS:GOSUB 16100:GOTO 600
100 CLS:CONTROL=0:FOR I=1 TO 3:B(I)=20:S(I)=2:V0(I)=0:Z0(I)=0:NEXT I
110 PRINT TAB(25);"OIL ANALYSIS - MASTER PROGRAM"
120 LOCATE 3,1:PRINT "System specification :-"
130 LOCATE 5,10:PRINT "Computer I / O connections"
140 LOCATE 7,20:PRINT "Parallel port - 1.  Printer"
150 LOCATE 8,20:PRINT "           or - 2.  Plotter"
160 LET A$=INKEY$:IF A$<"1" OR A$>"2" THEN 160 ELSE IF A$="1" THEN
CONTROL=CONTROL AND 254:A$(0)="Printer":ELSE
A$(0)="Plotter":CONTROL=CONTROL OR 1
170 LOCATE 7,36:PRINT A$(0)+"           "
180 LOCATE 8,20:PRINT "Serial Port   - Balance
"
190 CONTROL=CONTROL OR 2:A$(1)="Balance"
200 LET B$="COM1:2400,E,7,1,CS,DS,LF":LOCATE 9,1:PRINT "Command code
for balance. e.g. ";B$;:INPUT B$(0):IF B$(0)="" THEN B$(0)=B$
210 LET B$="T":LOCATE 10,1:PRINT "Command to make balance tare. e.g.
";B$;:INPUT B$(1):IF B$(1)="" THEN B$(1)=B$
220 LET B$="S":LOCATE 11,1:PRINT "Command to send stable reading. e.g.
";B$;:INPUT B$(2):IF B$(2)="" THEN B$(2)=B$
230 LOCATE 8,20:PRINT "Serial Port   - Balance
"+CHR$(34)+B$(0)+CHR$(34)+CHR$(44)+CHR$(34)+B$(1)+CHR$(34)+CHR$(44)+CH
R$(34)+B$(2)+CHR$(34)
240 FOR R=9 TO 11:LOCATE R,1:PRINT SPACE$(79):NEXT R
250 LOCATE 10,10:PRINT "Disk storage for data files"
260 LOCATE 12,20:INPUT "Drive:path e.g. C:\DATA\";A$
270 IF A$="" THEN A$(2)="A:":ELSE A$(2)=A$
280 LOCATE 12,20:PRINT "Path specified ";A$(2);"
"
```

```
390 LOCATE 14,10:PRINT "Titration type - 1.  B.N.
"
395 LOCATE 15,10:PRINT "            or - 2.  A.N. ?"
400 LET A$=INKEY$:IF A$<"1" OR A$>"2" THEN 400
404 LOCATE 15,10:PRINT "                                "
405 IF A$="1" THEN CONTROL=CONTROL OR 16:A$(4)="Direct B.N.":GOTO
414:ELSE CONTROL=CONTROL AND 239:A$(4)="A.N."
407 LOCATE 14,10:PRINT A$(4);" titration details.    "
410 LOCATE 15,20:PRINT " Titration type - 1.  Direct "
411 LOCATE 16,20:PRINT "             or - 2.  Back - ?"
412 LET A$=INKEY$:IF A$<"1" OR A$>"2" THEN 412
413 IF A$="2" THEN CONTROL=CONTROL OR 128:A$(4)=A$(4)+" Back -":ELSE
A$(4)="Direct "+A$(4):CONTROL=CONTROL AND 127
414 LOCATE 14,10:PRINT "Set-up for ";A$(4);" titration
"
450 LOCATE 15,10:PRINT "End-point detection - 1.  Conductimetric
"
460 LOCATE 16,10:PRINT "                      2.  Potentiometric
"
470 LET A$=INKEY$:IF A$<"1" OR A$>"2" THEN 470
480 IF A$="2" THEN CONTROL=CONTROL OR
64:A$(6)="Potentiometric":A$(5)="IP 177":ELSE CONTROL=CONTROL AND
191:A$(6)="Conductimetric":A$(5)="IP 400"
490 LOCATE 15,10:PRINT "       with ";A$(6);" end-point detection
"
500 LOCATE 16,10:PRINT "
"
505 LET A$="1":B=1
510 IF (CONTROL AND 16)=0 THEN 550
515 LOCATE 16,10:PRINT "Solvent system - 1.  ";A$(5)
520 LOCATE 17,10:PRINT "            or - 2.  IP 276"
530 LET A$=INKEY$:IF A$<"1" OR A$>"2" THEN 530
540 IF A$="2" THEN CONTROL=CONTROL OR 32:B=3:A$(5)="IP 276":ELSE
CONTROL=CONTROL AND 223
550 LOCATE 16,10:PRINT "       using ";A$(5);" specification solvent."
560 LOCATE 17,10:PRINT "
"
565 GOSUB 3000
570 LOCATE 22,1:PRINT "Should these values become the new default set-
up? Answer Y / N";
575 LET A$=INKEY$:IF A$="Y" OR A$="y" THEN 590:ELSE IF A$<>"N" AND
A$<>"n" THEN 575
580 LOCATE 22,1:PRINT "Use these values for this session only? Press
<SPACE> to confirm. Press either";
582 LOCATE 23,1:PRINT "<Esc> to use the current default set-up or
<ENTER> to modify the criteria.";
585 LET A$=INKEY$:IF A$=" " THEN 600 ELSE IF A$=CHR$(27) THEN 90
587 IF A$=CHR$(13) THEN 100 ELSE 585
590 GOSUB 16000
600 GOSUB 20000:IF CONTROL=0 THEN 100
602 SCREEN 0:COLOR 7,1:CLS:IF (CONTROL AND 32) THEN YINC=.2 ELSE
YINC=2
605 IF (CONTROL AND 8)=0 THEN 1000:ELSE PRINT A$(6);" ";A$(4);"
titration using ";A$(5);" specification solvent."
608 FOR I=1 TO 3:V(I)=V0(I):Z(I)=Z0(I):NEXT I
610 IF (B(1)+V(1)>18) AND (((CONTROL AND 48)=16) OR ((CONTROL AND
128)=128)) THEN B=1:GOSUB 13100
615 IF (B(2)+V(2)>18) AND ((CONTROL AND 16)=0) THEN B=2:GOSUB 13100
620 IF (B(3)+V(3)>18) AND ((CONTROL AND 48)=48) THEN B=3:GOSUB 13100
```

```
625 GOSUB 13200
630 LET V=V(1)+V(2)+V(3):Z=Z(1)+Z(2)+Z(3)
640 ERASE Y:DIM Y(Z)
650 LOCATE 3,1:PRINT USING "Mass of sample =##.### g. Add \     \
solvent and re-assemble the titrator.";M;A$(5)
655 LOCATE 5,1:PRINT "Check the stirrer power supply is ON then press
the space bar to continue."
660 WHILE INKEY$<>" ":WEND:LET BANDS = 191:OUT 772,BANDS
665 SCREEN 2:VIEW:CLS:PRINT USING "& & titration using & specification
solvent.";A$(6);A$(4);A$(5)
670 LOCATE 3,1:PRINT USING "Titrating##.### g of oil with up to##.###
mL in#### steps.                          ";M;V;Z
675 LOCATE 5,1:PRINT "Waiting until sensor is stable."
680 IF (CONTROL AND 64) THEN DELAY=300:GOSUB 13000
685 LET Z=0:V=0:XS=1:YS=YINC

690 LOCATE 24,51:PRINT USING "V =##.### mL    ";V/1000;
695 GOSUB 13500
705 IF Q>YS THEN YS=YS+YINC:GOTO 705
710 LOCATE 5,1:PRINT "                                              "
715 GOSUB 17200
720 LOCATE 24,1:PRINT "Press <Esc> to stop the titration.";
725 LOCATE 24,51:PRINT USING "V =##.### mL    G =###.### æS";V/1000;Q;
745 LET BT = TIMER:LT=0
750 FOR B=1 TO 3
752 FOR I=1 TO Z(B):J=0
755 IF INKEY$=CHR$(27) THEN 795
760 IF I>=11 THEN GOSUB 14500:IF (Y(I-1)>G(0,B) AND G>1) OR G>G(1,B)
THEN 795
765 GOSUB 13600:Z=Z+1:V=V+S(B):LOCATE 24,51:PRINT USING "V =##.###
mL";V/1000;
770 GOSUB 13500:IF V>1000*XS THEN XS=XS+1:J=1
775 IF Q>YS THEN YS=YS+YINC:J=1:GOTO 775
780 IF J=1 THEN GOSUB 17300:GOTO 787
785 LINE -(99+CINT(448*V/1000/XS),155-CINT(112*Q/YS))
786 LOCATE 24,66:PRINT USING "G =###.### æS";Q;
787 LET RT = TIMER - BT: IF RT < 0 THEN RT = RT + 86400!
788 LET DT = RT - LT: LT = RT
789 LOCATE 25,51:PRINT USING "Run time =#### s    ët =### s";RT;DT;
790 NEXT I
795 LET Z(B)=I-1:V(B)=Z(B)*S(B)/1000:B(B)=B(B)+V(B)
800 NEXT B:V=V/1000
805 LOCATE 3,1:PRINT USING "Titrating##.### g of oil with up to##.###
mL in#### steps.                          ";M;V;Z;
810 LET BANDS=63:OUT 772,BANDS:LOCATE 23,34:PRINT "Options :-"
820 LOCATE 24,1:PRINT "1 - Display graph.        2 - Table of results.
3 - Calculate B.N.       ";
825 IF DS=0 THEN LOCATE 25,1:PRINT "4 - Save data on disk.    5 - Run
new sample.        6 - Exit from program.    ";:GOTO 840
830 LOCATE 25,1:PRINT "4 - Data saved on disk.   5 - Run new sample.
6 - Exit from program.    ";
840 LET A$=INKEY$:IF A$<"1" OR A$>"6" THEN 840
850 ON VAL(A$) GOTO 870,890,895,900,910
855 SCREEN 0:COLOR 7,1:CLS:IF DS THEN 865 ELSE LOCATE 8,15:PRINT "Do
you want to save the current data? Answer Y / N."
860 LET A$=INKEY$:IF A$="n" OR A$="N" THEN 865:ELSE IF A$<>"y" AND
A$<>"Y" THEN 860
862 GOSUB 13800
```

```
865 CLS:LOCATE 10,14:PRINT "When you are ready to continue with the
next sample,"
867 LOCATE 12,28:PRINT "type 'RUN' or press 'F2'":LOCATE 1,1:END
870 GOSUB 14000:GOSUB 1100
880 GOTO 1040
890 SCREEN 0:COLOR 7,1:CLS:GOSUB 13700:LOCATE 12,14:PRINT "Do you want
to display the Base Number? Answer Y / N."
891 LET A$=INKEY$:IF A$="N" OR A$="n" THEN 893 ELSE IF A$<>"Y" AND
A$<>"y" THEN 891
892 LOCATE 12,13:PRINT "   Please wait. Base Number calculation in
progress.    ":GOSUB 18600
893 LPRINT CHR$(12);:GOTO 1040
895 GOSUB 18000:GOTO 1040
900 IF DS=0 THEN SCREEN 0:COLOR 7,1:CLS:GOSUB 13800:GOTO 1040:ELSE 840
910 SCREEN 0:COLOR 7,1:CLS:IF DS THEN 925 ELSE LOCATE 8,15:PRINT "Do
you want to save the current data? Answer Y / N."
915 LET A$=INKEY$:IF A$="n" OR A$="N" THEN 925:ELSE IF A$<>"y" AND
A$<>"Y" THEN 915
920 GOSUB 13800
925 CLS:LOCATE 10,29:PRINT "Run with a new sample.":GOSUB
14200:DS=0:LOCATE 12,19:PRINT "Is the system set-up correct? Answer Y
/ N."
930 LET A$=INKEY$:IF A$="n" OR A$="N" THEN 100:ELSE IF A$<>"y" AND
A$<>"Y" THEN 930
935 GOTO 600
1000 SCREEN 0:COLOR 7,1:CLS:LOCATE 10,27:PRINT "Retrieving data from
disk.":GOSUB 13900
1040 SCREEN 2:VIEW:CLS:GOSUB 17000
1050 GOTO 810
1100 '****** Hard copy main screen displays ******
1110 LOCATE 25,8:PRINT "Press space bar for hard copy - <Esc> to
continue with programme.";
1120 LET A$=INKEY$:IF A$=CHR$(27) THEN RETURN:ELSE IF A$<>CHR$(32)
THEN 1120
1130 CALL PRNSTAT(P%):WHILE P%<>144:LOCATE 25,5:PRINT "Check Printer
is switched on with paper in position, on-line and ready.";:CALL
PRNSTAT(P%):WEND
1140 LOCATE 25,1:PRINT SPACE$(78);
1150 LOCATE 3,10+(CONTROL AND 128)/4:PRINT "Sample name : ";SN$;
1160 LOCATE 4,10+(CONTROL AND 128)/4:PRINT "File : ";A$(7);
1170 LOCATE 25,10:IF V(1)<>0 THEN PRINT USING "Acid conc. =##.####
mol/L      ";C(1);:GOTO 1190
1180 LOCATE 25,10:IF V(3)<>0 THEN PRINT USING "Acid conc. =##.####
mol/L      ";C(3);
1190 IF V(2)<>0 THEN PRINT USING "Base conc. =##.#### mol/L";C(2);
1200 GOTO 15000
1999 END
3000 '****** Titrant details ******
3005 COL=17:IF (CONTROL AND 128) THEN COL=1:ELSE IF (CONTROL AND 16)=0
THEN 3105
3010 LOCATE 18,COL:PRINT "Parameters for Acid titrant              "
3015 LOCATE 19,COL:INPUT "Acid titrant conc.";C(B)
3020 IF C(B)=0 THEN C(B)=.1
3025 LOCATE 19,COL:PRINT USING "Acid titrant conc. = #.#### mol/L
";C(B)
3030 LOCATE 20,COL:INPUT "Max. volume of acid to add (mL)";V0(B)
3035 IF V0(B)=0 THEN V0(B)=5
3040 LOCATE 21,COL:INPUT "Volume increment (æL)";S(B)
3045 IF S(B)=0 THEN S(B)=20
```

```
3050 S=2:WHILE S<S(B):S=S+2:WEND:S(B)=S
3055 V=S(B):WHILE V<1000*V0(B):V=V+S:WEND:Z0(B)=V/S:V0(B)=V/1000
3060 LOCATE 22,COL:INPUT "Maximum gradient (æS/mL)";G(1,B)
3065 IF G(1,B)=0 THEN G(1,B)=100/10^B
3070 LOCATE 23,COL:INPUT "Maximum conductance (æS)";G(0,B)
3075 IF G(0,B)=0 THEN G(0,B)=180/10^B
3080 LOCATE 18,COL:PRINT USING "Add #.#### mol/L acid in### æL
steps";C(B);S(B)
3085 LOCATE 19,COL:PRINT USING "until V=##.### mL, dG/dV>##.##
æS/mL";V0(B);G(1,B)
3090 LOCATE 20,COL:PRINT USING "or G>###.## æS
";G(0,B)
3095 FOR I=21 TO 23:LOCATE I,COL:PRINT SPACE$(39);:NEXT I
3100 IF (CONTROL AND 128) THEN COL=41:ELSE 3200
3105 LOCATE 18,COL:PRINT "Parameters for Base titrant           "
3110 LOCATE 19,COL:INPUT "Base titrant conc.";C(2)
3115 IF C(2)=0 THEN C(2)=.1
3120 LOCATE 19,COL:PRINT USING "Base titrant conc. = #.#### mol/L
";C(2)
3125 LOCATE 20,COL:INPUT "Max. volume of base to add (mL)";V0(2)
3130 IF V0(2)=0 THEN V0(2)=5+2*V0(B)
3135 LOCATE 21,COL:INPUT "Volume increment (æL)";S(2)
3140 IF S(2)=0 THEN S(2)=20
3145 S=2:WHILE S<S(2):S=S+2:WEND:S(2)=S
3150 V=S(2):WHILE V<1000*V0(2):V=V+S:WEND:Z0(2)=V/S:V0(2)=V/1000
3155 LOCATE 22,COL:INPUT "Maximum gradient (æS/mL)";G(1,2)
3160 IF G(1,2)=0 THEN G(1,2)=1
3165 'IF CONTROL AND 128 THEN I=20:GOTO 3185:ELSE I=21
3170 LOCATE 23,COL:INPUT "Maximum conductance (æS)";G(0,2)
3175 IF G(0,2)=0 THEN G(0,2)=4
3180 LOCATE 20,COL:PRINT USING "or G>###.## æS
";G(0,2)
3185 LOCATE 18,COL:PRINT USING "Add #.#### mol/L base in### æL
steps";C(2);S(2)
3190 LOCATE 19,COL:PRINT USING "until V=##.### mL, dG/dV>##.##
æS/mL";V0(2);G(1,2)
3195 FOR I=21 TO 23:LOCATE I,COL:PRINT SPACE$(39);:NEXT I
3200 RETURN
13000 REM ***** timed delay subroutine *****
13010 LET T=TIMER
13020 WHILE (TIMER-T) < DELAY:WEND
13030 RETURN
13100 REM ***** refill burette *****
13110 LOCATE 3,1:PRINT "Refilling burette";B;"- please wait."
13120 OUT 772,BANDS-2^(2*B-1)
13130 DELAY = 1:GOSUB 13000
13140 OUT 772,BANDS
13150 WHILE (INP(773) AND 2^(B-1)):WEND
13160 LET B(B)=0
13170 RETURN
13200 REM ***** Sample mass from auto-balance *****
13210 OPEN B$(0) AS #1
13220 PRINT#1,B$(1)
13230 PRINT#1,B$(2)
13235 INPUT#1,M1$
13240 BEEP
13245 LOCATE 3,1:PRINT "Place empty vessel on balance pan
"
13250 PRINT#1,B$(2)
```

```
13255 INPUT#1,M2$
13260 WHILE (VAL(MID$(M2$,2))-VAL(MID$(M1$,2)))<25
13265 PRINT#1,B$(2)
13267 INPUT#1,M2$
13269 PRINT#1,B$(2):INPUT#1,M2$:WEND
13270 DELAY=2:GOSUB 13000
13275 PRINT#1,B$(2)
13277 INPUT#1,M2$
13280 BEEP
13285 LOCATE 3,1:PRINT "Now add oil sample to vessel
"
13290 PRINT#1,B$(2)
13295 INPUT#1,M3$
13300 WHILE (VAL(MID$(M3$,2))-VAL(MID$(M2$,2)))<.1
13305 PRINT#1,B$(2)
13310 INPUT#1,M3$
13315 WEND
13320 DELAY=5:GOSUB 13000
13325 PRINT#1,B$(2)
13330 INPUT#1,M3$
13335 LET M=VAL(MID$(M3$,2))-VAL(MID$(M2$,2))
13340 BEEP
13345 LOCATE 3,1:PRINT USING "Mass of oil taken for analysis =##.### g
";M
13350 CLOSE#1
13355 RETURN
13500 REM ***** Read DVM and calculate stable values *****
13510 DELAY=.5:FOR Q=1 TO 16-6*(CONTROL AND 32)/32
13520 GOSUB 13000:CALL DVM(V$):Q1=VAL(V$)
13530 LOCATE 24,66:PRINT USING "G =###.### æS";Q1/1000;:NEXT Q
13540 DELAY=1:GOSUB 13000:CALL DVM(V$):Q=VAL(V$)
13550 LOCATE 24,66:PRINT USING "G =###.### æS";Q/1000;
13560 IF ABS(Q-Q1)>4 THEN Q1=Q:GOTO 13540
13570 IF (CONTROL AND 64) THEN Q=Q/10000:ELSE Q=Q/1000
13580 LET Y(Z)=Q
13590 RETURN
13600 REM ***** Add S æl from piston burette B in 2 æl pulses *****
13610 FOR P=2 TO S(B) STEP 2
13620 OUT 772,BANDS-4^(B-1)
13630 DELAY=.05:GOSUB 13000
13640 OUT 772,BANDS
13650 DELAY=.05:GOSUB 13000
13660 NEXT P
13670 RETURN
13700 REM ***** Output data table to system printer *****
13705 LOCATE 10,18:PRINT "Printing table of results on system
printer."
13710 CALL PRNSTAT(P%):WHILE P%<>144:LOCATE 12,18:PRINT "Printer is
not responding - Clear the fault.";:CALL PRNSTAT(P%):WEND:LOCATE
12,18:PRINT SPACE$(45)
13715 LPRINT "Sample name : ";SN$;" File : ";A$(7):LPRINT
13716 IF V(1)<>0 THEN LPRINT USING "Acid conc. =##.### mol/L
";C(1);
13717 IF V(3)<>0 THEN LPRINT USING "Acid conc. =##.### mol/L
";C(3);
13718 IF V(2)<>0 THEN LPRINT USING "Base conc. =##.### mol/L";C(2);
13719 LPRINT:LPRINT
13720 LPRINT A$(6);" ";A$(4);"titration using ";A$(5);" specification
solvent."
```

```
13730 LPRINT:LPRINT USING "Titrating##.### g of oil with##.### mL
in#### steps.";M;V;Z
13740 LPRINT:LET S$=" V/mL     ":IF (CONTROL AND 64) THEN S$=S$+" E /
V":ELSE S$=S$+" G / uS"
13750 Q=(Z+1)/4:IF Q<>INT(Q) THEN Q=INT(Q)+1
13760 FOR COL=1 TO 61 STEP 20:LPRINT TAB(COL);S$;:NEXT COL:S$="##.###
":IF (CONTROL AND 64) THEN S$=S$+"##.####":ELSE S$=S$+"###.###"
13770 FOR ROW=1 TO Q:FOR COL=1 TO 61 STEP 20:I=ROW+Q*(COL-1)/20-1:IF
I<=Z(1) THEN LPRINT TAB(COL);:LPRINT USING S$;I*S(1)/1000;Y(I);:ELSE
IF I<=Z THEN LPRINT TAB(COL);:LPRINT USING S$;V(1)+(I-
Z(1))*S(2)/1000;Y(I);:ELSE 13790
13780 NEXT COL
13790 LPRINT:NEXT ROW:LPRINT:LPRINT:RETURN
13800 REM ***** Save data in specified file *****
13805 LOCATE 12,30:PRINT "Saving data on disk.";
13810 OPEN A$(7) FOR OUTPUT AS #1
13815 PRINT#1,SN$
13820 PRINT#1,CONTROL
13825 FOR B=1 TO 3
13830 PRINT#1,C(B);",";V(B);",";S(B);",";Z(B)
13835 NEXT B
13840 PRINT#1,M
13845 PRINT#1,A(1);",";A(2);",";A(3);",";A(4);",";A(5)
13850 FOR I=4 TO 6
13855 PRINT#1,A$(I)
13860 NEXT I
13865 FOR I=0 TO Z
13870 PRINT#1,Y(I)
13875 NEXT I
13880 CLOSE#1
13885 LET DS=-1
13890 RETURN
13900 REM ***** Retrieve data from specified file *****
13905 ERASE C,V,S,Z:DIM C(3),V(3),S(3),Z(3)
13910 OPEN A$(7) FOR INPUT AS #1
13915 INPUT#1,SN$
13920 INPUT#1,CONTROL
13925 LET Z=0:V=0:FOR B=1 TO 3
13930 INPUT#1,C(B),V(B),S(B),Z(B)
13935 Z=Z+Z(B):V=V+V(B):NEXT B
13940 INPUT#1,M:FOR I=1 TO 5:INPUT#1,A(I):NEXT I
13945 FOR I=4 TO 6
13950 INPUT#1,A$(I)
13955 NEXT I
13960 ERASE Y:DIM Y(Z)
13965 FOR I=0 TO Z
13970 INPUT#1,Y(I)
13975 NEXT I
13980 CLOSE#1
13985 IF (CONTROL AND 32) THEN YINC=.2 ELSE YINC=2
13990 IF A(4) THEN DS =-1 ELSE DS=0
13995 RETURN
14000 REM ***** Screen graphics routine *****
14010 SCREEN 2:VIEW:CLS
14020 LOCATE 1,1:PRINT USING "& & titration using##.### g of oil with
& solvent.";A$(6);A$(4);M;A$(5)
14030 DRAW "b m 59,12 d 160 r 560"
14040 XS=2*V:XS=(INT(XS)-(XS<>INT(XS)))/2
```

```
14050 FOR P=0 TO 5:DRAW "b m"+STR$(59+112*P)+",172 d 2":LOCATE
23,6+14*P:PRINT USING "##.##";P*XS/5;:NEXT P:LOCATE 24,42:PRINT
"V/ml";
14060 LET B=Y(0):FOR I=1 TO Z:IF Y(I)>B THEN B=Y(I)
14070 NEXT I
14080 YS=YINC:WHILE YS<B:YS=YS+YINC:WEND
14090 FOR P=0 TO 5:DRAW "b m 59,"+STR$(172-32*P)+" l 4":LOCATE 22-
4*P,1:PRINT USING "###.##";P*YS/5:NEXT P
14100 LOCATE 4,1:PRINT "G / æS"
14110 PSET (59,170-CINT(160*Y(0)/YS))
14120 LET J=0:TV=0:FOR B=1 TO 3:FOR I=1 TO Z(B):J=J+1:TV=TV+S(B)/1000
14130 LINE -(59+CINT(560*TV/XS),170-CINT(160*Y(J)/YS)):NEXT I:NEXT B
14140 RETURN
14200 REM ***** Check that interface m/c is intact *****
14210 RESTORE 40
14220 IF DVM<>64000! THEN 14300
14230 FOR I=0 TO 61
14240 READ P
14250 IF P<>PEEK(DVM+I) THEN 14300
14260 NEXT I
14270 RETURN
14300 CLS
14310 PRINT"Interface error"
14320 LOCATE 3,1:PRINT"current values :- DVM =";DVM
14330 RESTORE 40
14340 FOR I=0 TO 61
14350 PRINT USING "####";PEEK(64000!+I);
14360 NEXT I
14370 PRINT:PRINT
14380 PRINT "Correct values :- DVM =";64000!
14390 FOR I=0 TO 61
14400 READ P:PRINT USING "####";P;
14410 NEXT I
14420 PRINT:PRINT"You may continue by typing 'CONT' if you wish"
14430 END
14440 RETURN
14499 END
14500 '****** Calculate gradient of titration curve ******
14510 LET G=0
14520 FOR K=0 TO 10
14530 LET G=G+(5-K)*Y(Z-K)
14540 NEXT K
14550 LET G=G/.11/S(B)
14560 RETURN
15000 REM ***** Screen dump routine *****
15010 LCOPY:LPRINT CHR$(12);:RETURN
16000 '****** Create a default file ******
16010 OPEN "DEFAULT.SEQ" FOR OUTPUT AS #1
16020 PRINT#1,CONTROL
16030 FOR I=0 TO 7:PRINT#1,A$(I):NEXT I
16040 FOR I=0 TO 2:PRINT#1,B$(I):NEXT I
16060 FOR I=1 TO 3:PRINT#1,C(I);",";V0(I);",";S(I);",";Z0(I);
16070 FOR J=0 TO 1:PRINT#1,;",";G(J,I);:NEXT J:PRINT#1,:NEXT I
16080 CLOSE#1
16090 RETURN
16100 '****** Read from the default file ******
16110 OPEN "DEFAULT.SEQ" FOR INPUT AS #1
16120 INPUT#1,CONTROL
16130 FOR I=0 TO 7:INPUT#1,A$(I):NEXT I
```

```
16140 FOR I=0 TO 2:LINE INPUT#1,B$(I):NEXT I
16160 FOR I=1 TO 3:INPUT#1,C(I),V0(I),S(I),Z0(I),G(0,I),G(1,I):NEXT I
16170 CLOSE#1
16180 RETURN
17000 '****** Plot data in graphics window ******
17010 LOCATE 1,1:PRINT USING "& & titration using & specification
solvent.";A$(6);A$(4);A$(5)
17020 LOCATE 3,1:PRINT USING "Titrating##.### g of oil with##.### mL
in#### steps.";M;V;Z
17030 B=Y(0)
17032 FOR I=1 TO Z
17034 IF Y(I)>B THEN B=Y(I)
17036 NEXT I
17038 YS=YINC:WHILE YS<B:YS=YS+YINC:WEND
17040 XS=INT(V)-(V<>INT(V))

17050 VIEW SCREEN (55,29)-(584,171),,1
17060 DRAW "b m 95,43 r 4 d 56 l 4 r 4 d 56 l 4 r 4 d 2 u 2 r 224 d 2
u 2 r 224 d 2":LOCATE 5,34:PRINT "Titration Curve"
17070 FOR Y=0 TO 2:LOCATE 20-7*Y,9:PRINT USING "##.#";Y*YS/2:NEXT
Y:LOCATE 9,9:PRINT "G/æS"
17080 LOCATE 21,12:PRINT USING "##";0:LOCATE 21,40:PRINT USING
"#.#";XS/2:LOCATE 21,68:PRINT USING "##";XS:LOCATE 21,53:PRINT "V/mL";
17090 PSET (99,155-CINT(112*Y(0)/YS))
17100 LET J=0:TV=0:FOR B=1 TO 3:FOR I=1 TO
1000*V(B)/S(B):J=J+1:TV=TV+S(B)/1000
17110 LINE -(99+CINT(448*TV/XS),155-CINT(112*Y(J)/YS)):NEXT I:NEXT B
17120 RETURN
17200 '****** Create graphics window ******
17210 VIEW SCREEN (55,29)-(584,171),,1
17220 DRAW "b m 95,43 r 4 d 56 l 4 r 4 d 56 l 4 r 4 d 2 u 2 r 224 d 2
u 2 r 224 d 2":LOCATE 5,34:PRINT "Titration Curve"
17230 FOR Y=0 TO 2:LOCATE 20-7*Y,9:PRINT USING "##.#";Y*YS/2:NEXT
Y:LOCATE 9,9:PRINT "G/æS"
17240 LOCATE 21,12:PRINT USING "##";0:LOCATE 21,40:PRINT USING
"#.#";XS/2:LOCATE 21,68:PRINT USING "##";XS:LOCATE 21,53:PRINT "V/mL";
17250 PSET (99,155-CINT(112*Q/YS))
17260 RETURN
17300 '****** Re-scale graphics window ******
17310 VIEW SCREEN (100,43)-(548,154):CLS
17320 FOR Y=0 TO 2:LOCATE 20-7*Y,9:PRINT USING "##.#";Y*YS/2:NEXT Y
17330 LOCATE 21,12:PRINT USING "##";0:LOCATE 21,40:PRINT USING
"#.#";XS/2:LOCATE 21,68:PRINT USING "##";XS;
17340 PSET (99,155-CINT(112*Y(0)/YS))
17350 LET J=0:TV=0:FOR BB=1 TO 3:FOR II=1 TO
1000*V(BB)/S(BB):J=J+1:TV=TV+S(BB)/1000
17360 LINE -(99+CINT(448*TV/XS),155-CINT(112*Y(J)/YS)):IF J>=Z THEN
17380
17370 NEXT II:NEXT BB
17380 RETURN
17400 '****** Display fitted curve and data points ******
17410 SCREEN 2:VIEW:CLS
17420 LOCATE 1,1:PRINT USING "& & titration using##.### g of oil with
& solvent.";A$(6);A$(4);M;A$(5)
17430 DRAW "b m 59,12 d 160 r 560"
17440 XS=2*V:XS=(INT(XS)-(XS<>INT(XS)))/2
17450 FOR P=0 TO 5:DRAW "b m"+STR$(59+112*P)+",172 d 2":LOCATE
23,6+14*P:PRINT USING "##.##";P*XS/5;:NEXT P:LOCATE 24,42:PRINT
"V/mL";
```

```
17460 B=Y(0):FOR I=1 TO Z:IF Y(I)>B THEN B=Y(I)
17470 NEXT I

17480 YS=YINC:WHILE YS<B:YS=YS+YINC:WEND
17490 FOR P=0 TO 5:DRAW "b m 59,"+STR$(172-32*P)+" l 4":LOCATE 22-
4*P,1:PRINT USING "###.##";P*YS/5:NEXT P
17500 LOCATE 12,1:PRINT " G / æS"
17510 LET J=0:TV=0:FOR B=1 TO 3:FOR I=1 TO Z(B):J=J+1:TV=TV+S(B)/1000

17520 PSET (63+CINT(560*TV/XS),170-CINT(160*Y(J)/YS)):DRAW "l 8 r 4 u
2 d 4":NEXT I:NEXT B
17530 LET X=EXP((0-A(4))/A(5)):Y=A(1)+A(3)*LOG((X+1/X)/2):PSET
(59,170-CINT(160*Y/YS))
17540 FOR P=1 TO 560:X=P*XS/560:IF X>TV THEN 17560
17550 Y=A(1)+A(2)*X:X=EXP((X-A(4))/A(5)):Y=Y+A(3)*LOG((X+1/X)/2):LINE
-(59+P,170-CINT(160*Y/YS)):NEXT P
17560 RETURN
17600 '****** Display first derivative of fitted function ******
17610 SCREEN 2:VIEW:CLS
17612 LOCATE 1,1:PRINT "dG";:GET (0,0)-(15,7),X%:PUT (16,52),X%:LOCATE
1,1:PRINT "  ";
17614 PSET (0,0):LINE -(15,0):GET (0,0)-(15,7),X%:PUT
(16,60),X%:LOCATE 1,1:PRINT "  ";
17616 LOCATE 1,1:PRINT "dV";:GET (0,0)-(15,7),X%:PUT (16,62),X%:LOCATE
1,1:PRINT "  ";
17620 LOCATE 1,1:PRINT USING "& & titration using##.### g of oil. 1st.
derivative.";A$(6);A$(4);M
17630 DRAW "b m 59,12 d 160 r 560"
17640 XS=2*V:XS=(INT(XS)-(XS<>INT(XS)))/2
17650 FOR P=0 TO 5:DRAW "b m"+STR$(59+112*P)+",172 d 2":LOCATE
23,6+14*P:PRINT USING "##.##";P*XS/5;:NEXT P:LOCATE 24,42:PRINT
"V/mL";
17660 LET B=A(2)+A(3)/A(5)*SGN(A(5))
17670 YS=YINC:WHILE YS<B:YS=YS+YINC:WEND
17680 FOR P=0 TO 5:DRAW "b m 59,"+STR$(172-32*P)+" l 4":LOCATE 22-
4*P,1:PRINT USING "###.##";P*YS/5:NEXT P
17690 LOCATE 12,1:PRINT " æS/mL "
17700 LET X=EXP((0-A(4))/A(5)):Y=A(2)+A(3)*(X-1/X)/(X+1/X)/A(5):PSET
(59,170-CINT(160*Y/YS))
17710 FOR P=1 TO 560:X=P*XS/560:X=EXP((X-A(4))/A(5)):Y=A(2)+A(3)*(X-
1/X)/(X+1/X)/A(5):LINE -(59+P,170-CINT(160*Y/YS)):NEXT P
17720 RETURN
17800 '****** Display second derivative of fitted function ******
17810 SCREEN 2:VIEW:CLS
17812 LOCATE 1,1:PRINT "dýG";:GET (0,0)-(23,7),X%:PUT (8,52),X%:LOCATE
1,1:PRINT "   ";
17814 PSET (0,0):LINE -(23,0):GET (0,0)-(23,7),X%:PUT (8,60),X%:LOCATE
1,1:PRINT "   ";
17816 LOCATE 1,1:PRINT "dVý";:GET (0,0)-(23,7),X%:PUT (8,62),X%:LOCATE
1,1:PRINT "   ";
17820 LOCATE 1,1:PRINT USING "& & titration using##.### g of oil. 2nd.
derivative.";A$(6);A$(4);M
17830 DRAW "b m 59,12 d 160 r 560"
17840 XS=2*V:XS=(INT(XS)-(XS<>INT(XS)))/2
17850 FOR P=0 TO 5:DRAW "b m"+STR$(59+112*P)+",172 d 2":LOCATE
23,6+14*P:PRINT USING "##.##";P*XS/5;:NEXT P:LOCATE 24,42:PRINT
"V/mL";
17860 B=A(3)/A(5)/A(5)
17870 YS=YINC:WHILE YS<B:YS=YS+YINC:WEND
```

```
17880 FOR P=0 TO 5:DRAW "b m 59,"+STR$(172-32*P)+" l 4":LOCATE 22-
4*P,1:PRINT USING "###.##";P*YS/5:NEXT P
17890 LOCATE 12,1:PRINT "æS/mLý "
17900 LET X=EXP((0-A(4))/A(5)):Y=A(3)*(2/(X+1/X)/A(5))^2:PSET (59,170-
CINT(160*Y/YS))
17910 FOR P=1 TO 560:X=P*XS/560:X=EXP((X-
A(4))/A(5)):Y=A(3)*(2/(X+1/X)/A(5))^2:LINE -(59+P,170-
CINT(160*Y/YS)):NEXT P
17920 RETURN
18000 '****** Calculate Base Number for IP 400 titration ******
18010 SCREEN 0:COLOR 7,1:CLS
18020 LOCATE 1,1:PRINT "Calculating Base Number - IP400 titration."
18030 LOCATE 3,6:PRINT "Estimating gradient and curvature."
18035 LOCATE 4,6:PRINT "Please wait."
18040 GOSUB 19100:LOCATE 3,6:PRINT "Using estimated values of the
gradient,"
18045 LOCATE 4,6:PRINT "Method (1) - Maximum curvature gives :- "
18050 LOCATE 5,19:PRINT USING "End-point at##.## mL       B.N. =###.#
mg KOH/g";X;56.1*C(1)*X/M
18055 LOCATE 7,6:PRINT "Method (2) - Line intersection gives :- "
18060 LOCATE 8,19:PRINT USING "End-point at##.## mL       B.N. =###.#
mg KOH/g";Y;56.1*C(1)*Y/M
18065 LOCATE 10,6:PRINT "Least squares fitting the titration curve."
18070 LOCATE 11,6:PRINT "Please wait.";
18080 IF A(4)<>0 THEN 18190
18090 LET II=0:DS=0:A$=""
18100 GOSUB 19200
18110 LET II=II+1
18120 LOCATE 11,18:PRINT USING " Performing iteration ##.";II:GOSUB
19300
18130 IF II=10 AND S<>0 THEN GOSUB 19220
18140 IF II=20 AND S<>0 THEN LET S=1:FOR I=1 TO 5:A(I)=0:NEXT I:LET
A$="Maximum number of iterations exceeded.  "
18150 ON S+2 GOTO 18110,18190,18160
18160 LOCATE 11,6:PRINT A$
18170 LOCATE 12,6:PRINT "Press any key to continue.";
18180 WHILE INKEY$="":WEND:RETURN
18190 LOCATE 10,6:PRINT "Titration curve fitted by non-linear least
squares."
18200 LOCATE 11,6:PRINT "Method (3) - Curve fitting gives :-      ";
18205 LOCATE 12,19:PRINT USING "End-point at##.## mL       B.N. =###.#
mg KOH/g";A(4);56.1*C(1)*A(4)/M
18210 LOCATE 14,11:PRINT "Press <Esc> to continue with the main
programme,"
18220 LOCATE 16,19:PRINT "0 - to view the fitted curve,"
18230 LOCATE 18,19:PRINT "1 - to view the first derivative,"
18240 LOCATE 20,19:PRINT "2 - to view the second derivative."
18250 LET A$=INKEY$:IF A$=CHR$(27) THEN RETURN ELSE IF A$<"0" OR
A$>"2" THEN 18250
18260 ON (VAL(A$)+1) GOSUB 17400,17600,17800
18270 GOSUB 1100
18280 SCREEN 0:COLOR 7,1:CLS:LOCATE 7,6:PRINT "Base Number
Calculations - IP400 titration.":GOTO 18190
18600 '****** Print Base Number results for IP 400 titration ******
18610 LPRINT "Using estimated values of the gradient,"
18620 LPRINT "Method (1) - Maximum curvature gives :- "
18630 GOSUB 19100
18640 LPRINT USING "            End-point at##.## mL       B.N.
=###.# mg KOH/g";X;56.1*C(1)*X/M
```

```
18650 LPRINT "Method (2) - Line intersection gives :- "
18660 LPRINT USING "              End-point at##.## mL       B.N.
=###.# mg KOH/g";Y;56.1*C(1)*Y/M
18670 IF A(4)<>0 THEN 18790
18680 LET II=0:DS=0:A$=""
18690 GOSUB 19200
18700 LET II=II+1
18710 GOSUB 19300
18720 IF II=10 AND S<>0 THEN GOSUB 19220
18730 IF II=20 AND S<>0 THEN LET S=1:FOR I=1 TO 5:A(I)=0:NEXT I:LET
A$="Maximum number of iterations exceeded.  "
18740 ON S+2 GOTO 18700,18790,18750
18750 LPRINT "When non-linear least squares fitting the titration
curve,"
18760 LPRINT A$
18770 RETURN
18790 LPRINT "Titration curve fitted by non-linear least squares."
18800 LOCATE 11,6:PRINT "Method (3) - Curve fitting gives :-";
18810 LPRINT USING "              End-point at##.## mL       B.N.
=###.# mg KOH/g";A(4);56.1*C(1)*A(4)/M
18820 RETURN
19100 '****** Calculate gradient and curvature ******
19110 ERASE D,R:DIM D(5,Z),R(Z)
19120 LET B=Z-3:FOR I=3 TO B:S1=0:S2=0
19130 FOR J=-3 TO 3:S1=S1+Y(I+J):S2=S2+J*Y(I+J):NEXT J
19140 IF I=3 OR I=B THEN D(0,I)=S1/7:D(0,I+1)=S2/28
19150 LET D(1,I)=S2/28:NEXT I
19160 FOR I=3 TO Z-4:IF D(1,I)>D(0,Z-2)/2 THEN B=I:I=Z
19170 NEXT I
19180 LET X=B*S(1)/1000
19190 LET C=CINT((D(0,Z-2)*(Z-3)-D(0,4)*3-D(0,Z-3)+D(0,3))/(D(0,Z-2)-
D(0,4))):Y=C*S(1)/1000
19199 RETURN
19200 LET A(4)=X:GOTO 19230
19210 '****** Set initial estimates for non-linear least squares
******
19220 LET A(4)=Y
19230 LET A(5)=.1*(X+Y)^(3/7):A(3)=0:A(2)=0:A(1)=0
19240 FOR I=0 TO Z:D(1,I)=1:D(2,I)=I*S(1)/1000:NEXT I
19250 LET NE=3
19260 RETURN
19300 '****** Carry out curve fitting procedure ******
19310 FOR I=0 TO Z
19320 LET S=(D(2,I)-A(4))/A(5):X=EXP(S):X1=1/X:COSH=X+X1:TANH=(X-
X1)/COSH:D(3,I)=LOG(COSH/2):R(I)=Y(I)-A(1)-A(2)*D(2,I)-A(3)*D(3,I)
19325 IF NE>3 THEN D(4,I)=-A(3)/A(5)*TANH:D(5,I)=S*D(4,I)
19330 NEXT I
19340 FOR J=1 TO NE:W(J)=0:FOR K=J TO NE:X(J,K)=0:FOR I=0 TO
Z:X(J,K)=X(J,K)+D(J,I)*D(K,I):NEXT I:IF J<>K THEN X(K,J)=X(J,K)
19350 NEXT K:FOR I=0 TO Z:W(J)=W(J)+D(J,I)*R(I):NEXT I:NEXT J
19360 FOR I=1 TO NE
19370 IF ABS(X(I,I))>1E-10 THEN 19500
19380 FOR K=I+1 TO NE
19390 IF ABS(X(K,I))<1E-10 THEN 19440
19400 LET S=W(K):W(K)=W(I):W(I)=S
19410 FOR J=NE TO I STEP -1
19420 LET S=X(K,J):X(K,J)=X(I,J):X(I,J)=S
19430 NEXT J:GOTO 19500
19440 NEXT K
```

```
19450 LET A$="The least squares normal matrix is singular."
19460 FOR J=1 TO 5:A(J)=0:NEXT J
19470 LET S=1:DS=0
19480 GOTO 19690
19500 FOR K=I+1 TO NE
19510 LET W(K)=W(K)-X(K,I)*W(I)/X(I,I)
19520 FOR J=NE TO I STEP -1
19530 LET X(K,J)=X(K,J)-X(K,I)*X(I,J)/X(I,I)
19540 NEXT J
19550 NEXT K
19560 NEXT I
19570 FOR I=NE TO 1 STEP -1
19580 LET E(I)=W(I)
19590 FOR J=I+1 TO NE
19600 LET E(I)=E(I)-X(I,J)*E(J)
19610 NEXT J
19620 LET E(I)=E(I)/X(I,I)
19630 NEXT I
19640 LET S=0
19650 FOR I=1 TO NE
19660 LET A(I)=A(I)+E(I)
19670 IF ABS(E(I))>.0001 THEN S=-1
19680 NEXT I
19690 LET NE=5:RETURN
20000 '****** Type of run ******
20010 CLS:LOCATE 1,10:PRINT "Type of run required :-"
20020 LOCATE 3,10:PRINT "          1. - Perform titration;"
20025 LOCATE 5,10:PRINT "          2. - Retrieve stored data;"
20030 LOCATE 7,10:PRINT "          3. - Input new set-up parameters;"
20035 LOCATE 9,10:PRINT "          4. - Prime burette(s);"
20036 LOCATE 11,10:PRINT "          5. - Run the service pack;"
20037 LOCATE 13,10:PRINT "          6. - Check solution
concentrations;"
20038 LOCATE 15,10:PRINT "       or 7. - End programme."
20040 LET A$=INKEY$:IF A$<"1" OR A$>"7" THEN 20040
20043 IF A$="7" THEN 865
20044 IF A$="6" THEN GOSUB 25000:GOTO 20000
20045 IF A$="5" THEN CHDIR "SERVICE":RUN "SELECT"
20046 IF A$="4" THEN GOSUB 20300:GOTO 20000
20050 IF A$="1" THEN CONTROL=CONTROL OR 8:A$(3)="titration":ELSE IF
A$="2" THEN A$(3)="retrieve stored data":CONTROL=CONTROL AND 247:ELSE
CONTROL=0:RETURN
20060 LOCATE 1,30:PRINT " - ";A$(3);"                    "
20070 FOR R=3 TO 15 STEP 2:LOCATE R,10:PRINT SPACE$(69):NEXT R
20080 IF (CONTROL AND 8) THEN A$(7)="for":GOTO 20130:ELSE A$(7)="of"
20090 LOCATE 3,10:PRINT "Name ";A$(7);" data file
":LOCATE 3,29:INPUT A$
20100 IF A$="" THEN LOCATE 4,1:FILES A$(2)+"*.seq":GOTO 20090
20110 A$(7)=A$(2)+A$+".SEQ":LOCATE 3,29:PRINT A$(7);"
"
20120 RETURN
20130 LET A$=CHR$(64+VAL(RIGHT$(DATE$,4))-
1980)+CHR$(64+VAL(LEFT$(DATE$,2)))+MID$(DATE$,4,2)+LEFT$(TIME$,2)+MID$
(TIME$,4,2)
20140 LOCATE 3,10:PRINT "Name ";A$(7);" data file
":LOCATE 3,29:INPUT A$(7)
20150 IF A$(7)<>"" THEN A$=A$(7)
20160 A$(7)=A$(2)+A$+".SEQ":LOCATE 3,29:PRINT A$(7);"
"
```

```
20170 LOCATE 5,10:INPUT "Sample name";SN$
20180 LOCATE 5,10:PRINT "Sample name : ";SN$;"
"
20190 LET DS=0:A(4)=0
20200 RETURN
20300 REM ******** PRIME BURETTES ******
20310 CLS:LOCATE 1,10:PRINT "Which burette is required?"
20315 LET B=0
20320 LOCATE 3,5:PRINT "Input 1 for base number titrant or 2 for acid
number titrant"
20330 LET A1$=INKEY$:IF A1$<"1" OR A1$>"2" THEN 20330
20340 IF A1$="1" THEN B=1
20350 IF A1$="2" THEN B=2
20353 LET C=0
20358 LOCATE 3,5:PRINT "Place vessel under burette ";A1$;" - press
space bar when ready to proceed"
20359 LET A2$=INKEY$:IF A2$<>" " THEN 20359
20360 LOCATE 3,5:PRINT "Priming burette ";A1$;"
";
20365 LOCATE 9,1: PRINT SPACE$(79);:LOCATE 5,5-6*(C<>0):INPUT "Volume
(in mL) to be displaced";V
20370 FOR P=2 TO 1000*V STEP 2
20375 LOCATE 6,5:PRINT USING "Total volume delivered =##.###
mL";P*.001+C
20380 OUT 772,BANDS-4^(B-1)
20390 DELAY=.05:GOSUB 13000
20400 OUT 772,BANDS
20410 DELAY=.05:GOSUB 13000
20420 NEXT P
20430 LOCATE 9,1:PRINT "Do you want to reprime this burette? Answer Y
/ N."
20440 LET A$=INKEY$:IF A$="y" OR A$="Y" THEN C=C+V:LOCATE 5,5:PRINT
"Extra ";:GOTO 20365:ELSE IF A$<>"n" AND A$<>"N" THEN 20440
20445 CLS:GOSUB 13110
20450 CLS
20470 LOCATE 8,15:PRINT "Do you want to prime another burette? Answer
Y / N."
20480 LET A$=INKEY$:IF A$="y" OR A$="Y" THEN 20300:ELSE IF A$<>"n" AND
A$<>"N" THEN 20480
20490 RETURN
25000 RETURN
```

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Fourier Transform Infrared Spectroscopy and Multivariate data Analysis Approach for Differentiation between 'Good' 'Borderline' and 'Poor' ASTM Lubricant Standards by Ring Zone Sampling

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Introduction

The performance of three formulated lubricants in the top ring zone of a Petter W-1 gasoline engine is at the centre of this investigation. Top ring zone sampling is a simple, rapid and low cost engine test method for the study oil degradation. Using ring zone sampling coupled with chemical/physical measurements and the application of chemometric methods, the differences between the performance levels of the three formulated lubricants was established. The three lubricants were formulated to specific performance standards: 'Good lubricant' (formulated to pass ASTM Sequence IIIE/VG test), 'Borderline lubricant' (formulated to provide average results to ASTM Sequence IIIE/VG test), 'Poor lubricant' (formulated to fail ASTM Sequence IIIE/VG test). The lubricants were sampled from behind the piston ring at hourly intervals over a twenty-five hour test run. The chemical/physical measurement of the used oil samples identified the relative degradation of the samples. With the use of some chemometric methods the differences in performance levels of the three sets of lubricants are illustrated.

Method and Materials

The three formulated oil samples were tested on a Petter type W-1 gasoline engine, with a single cylinder, side valve and glycol-cooled. The used oil samples were collected via Teflon PolyTetraFluoroEthylene (PTFE) tubing connected behind the top piston ring, at hourly intervals over a twenty-five hour test run. The collected samples were subsequently analysed by chemical/physical measurements.

Fig1. Picture of a piston ring with a Teflon PTFE tubing connected behind the top of the piston ring

Fourier transform Infrared spectroscopy (FTIR) was used to detect oil contaminants (water, soot, glycol, and fuels) depletion of additives and increase in oxidation and nitration products.

Thermo gravimetric analyser (TGA) and Micro-viscometer were used to determine the volatility and viscosity of the lubricating oils respectively.

Principal component analysis (PCA) - applied to the FTIR data of all three sets of lubricant, to evaluate its ability to differentiate the three types of oils based on the degradation condition of the used oil samples.

Quality Control Charts – used to monitor the parameters which indicate the degradation condition of the used oil samples over the twenty five hour engine test run.

Partial least squares discriminant analysis (PLSDA) – used to establish a 'class membership' model for each type of lubricating oil based on their degradation .

Results

Principal Component Score plot

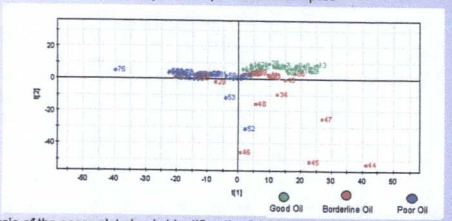

Fig 2. Analysis of the score plot clearly identifies the 3 types of lubricating oil samples. The Good oil samples are observed as a unified group in the first quadrant, majority of the poor oil samples are formed in the second quadrant, while the borderline oil samples spread between the good and poor oils.

First principal components loading plots

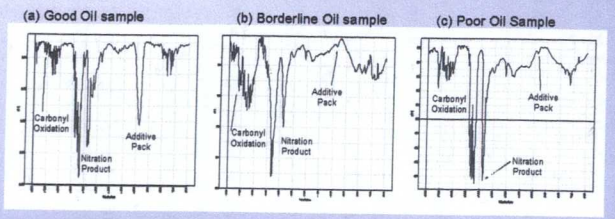

Fig.3(a-c). The PCA algorithm is used to translate part of the infrared region where oil degradation occurs. The difference between the performances of the formulated oil samples is shown. The depletion of additive properties from 'Good' to 'Poor' oils is identified by the distinctively long peak at 978 cm^{-1} in the first plot, but significantly reduced in the other plots. Increase in oxidation and nitration products from good to poor oils is identified by peaks at 1722 and 1376 cm^{-1} respectively.

Condition monitoring by control charts

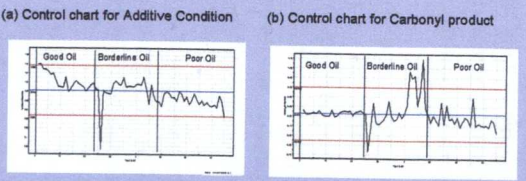

Fig 4 (a-b). Close monitoring Of the additive and carbonyl Variables clearly shows the difference between the three samples

PLSDA Score and Loading plots

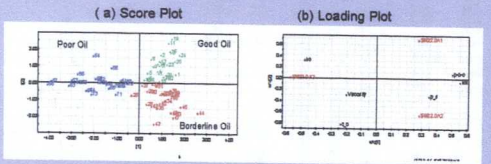

Fig 5(a-b). The PLSDA plots evidently show the differences between the three formulated lubricant oils. The enhanced differentiation between the oil samples is facilitated by the degradation variables in the loading plots.

Conclusion

The results present a detailed insight into differences between the performance level of the three formulated lubricating oils. The performance of the oils is as anticipated.

- Good oil formulation: the stability of this oil is exhibited as a distinct cohesive group in the PCA score plot. The formulated properties of this sample allows it to sufficiently endure the severe degradative conditions of the piston ring grove for the entire test run.
- Borderline oil formulation: initial results show slow degradation of the oil, after the first 15hours the oil degraded rapidly and could no longer withstand the severe engine conditions. The properties are suggested to be sufficient for the first half of the test run.
- Poor oil formulation: the sample is incapable of surviving the engine conditions. This oil suffers extensive degradation as the results show. The small peaks of additive properties in the loading plot suggest loss of additive performance and an increase in contamination occurring. The PLSDA plots confirms that this sample is typical of properties associated with degradative conditions such as increased viscosity, carbonyl, nitration products and low additives.

The project confirms the feasibility of:

- using ring zone sampling to obtain degraded oil samples in a short timescale
- FTIR chemical analysis gives excellent indication of oil degradation conditions
- chemometric methods provide detailed and visual insights about the conditions and performances of the used oil samples.

The method is more

- Rapid
- Cost effective
- informative

Compared with previous studies

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